# Transport Properties of Gases and Gaseous Mixtures at High Temperatures\*

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Thermal conductivity data as a function of temperature recently obtained by the conductivity column method for monatomic gases (helium, neon, argon, krypton, and xenon), diatomic gases (hydrogen, deuterium, nitrogen, oxygen, carbon monoxide) and triatomic gases (nitrous oxide and carbon dioxide) have been interpreted according to the principle of corresponding states. It is found that data for all the monatomic gases lie on a single reduced plot of  $M^{1/2}P_c^{-2/3}T_c^{1/6}k$ versus  $T/T_c$ , while the data for diatomic gases and carbon dioxide cluster along two different curves. Here  $M, P_c, T_o, T$  and k are the molecular weight, critical pressure, critical temperature, temperature, and coefficient of thermal conductivity of the gas, respectively. This has enabled us to estimate k values for neon, argon, krypton, and xenon over a wider temperature range than available from direct measurements.

The directly measured thermal conductivity data on twelve gases are represented successively by linear, quadratic, and cubic polynomials in temperature. The linear form is found inadequate, while for the present temperature range, the quadratic and cubic polynomials are about equally adequate. It has also been pointed out as to how the conductivity data on polar and nonpolar gases can be reduced from one temperature to another, and the function occurring in the expression for the temperature coefficient of thermal conductivity is tabulated for the Lennard-Jones (12-6) and (12-6-3) intermolecular potentials.

The procedures which may enable the determination of thermal conductivity of multicomponent mixtures from the known values for pure gases have been pointed out and briefly described. How this knowledge of thermal conductivity can help in estimating the two other transport properties (viscosity and diffusion) of pure gases and multicomponent mixtures is discussed. In conclusion, this study is aimed at facilitating the estimation of transport properties of gases and gaseous mixtures at moderate and even high temperatures until dissociation and ionization effects appear, but only at ordinary pressures, i.e., about one atmo-

### INTRODUCTION

The knowledge of the transport properties of gases and gaseous mixtures at high temperatures is necessary for various applied design problems as well as for the determination of inter-molecular forces. The measurement of thermal conductivity, viscosity or diffusion coefficients becomes increasingly difficult as the temperature of the test material is increased and very few reliable techniques are known which can be used beyond 1000°C. The framework of kinetic theory is well developed (1, 2) and

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reliable calculations are possible if the collision cross sections are known with enough accuracy. Amdur and Mason (3) adopted this procedure and evaluated the transport properties basing their estimates of collision integrals on the intermolecular forces determined from experiments on scattering of molecular beams of neutral particles (4, 5).

Work on the measurement of thermal conductivity of rare gases (6–8) by the shock tube technique has shown that Amdur and Mason values (3) are overestimates. It may also be mentioned that the shock tube method for determining the thermal conductivity of gases introduced by Smiley (9), needs to be carefully evaluated in the light of recent theoretical (10) and experimental (11) developments. The partial insensitivity of the method to determine the thermal conductivity of gases as a function of temperature is not difficult to see (12) and indeed many earlier workers (13–15) have consequently preferred to determine the integral of thermal conductivity instead. Matula (16) has recently employed this very technique and determined also the thermal conductivity of argon-helium mixture in the temperature range 650–5000°K. These measurements (16) have also provided an opportunity to compare (17) the results (16) as obtained from the shock tube method at the lower end of the temperature range with the data obtained from more established techniques.

Carnevale and co-workers (18, 19) have used the measurement of the attenuation of ultrasonic pulses in heated gases (3000–15,000°K) to determine viscosity and thermal conductivity. Interpretation at high temperatures gets so involved that reliable determination of transport coefficients is questionable. Ahtye (20) has examined this problem in detail and has presented a very useful evaluation of the technique and complications which will result from chemical relaxation and radiative heat transfer at high temperatures. These effects enhance by several times the observed absorption of the classical absorption due to viscosity and thermal conductivity.

Blais and Mann (21) suggested a procedure for measuring the thermal conductivity of gases by using a hot-wire column and this can be employed for temperatures above 1000°C. Timrot and Umanskii (22) have reported measurements up to 2400°K. Saxena and coworkers (23-31) have extensively used this column method (21) for the measurement of thermal conductivity as a function of temperature up to about 1500°K. The purpose of this paper is to pool all these data together and develop, through the application of the principle of corresponding states, the most probable values of thermal conductivity, as a function of temperature, of gases in the ground state. The question of the empirical laws governing the temperature variation of thermal conductivity is considered both theoretically as well as from experimental data. It is also pointed out, how best values for the thermal conductivity of binary and multicomponent mixtures of gases can be generated as a function of temperature and for various compositions of the mixture. From these conductivity values, it is also possible to at least approximately determine the other two transport coefficients (viscosity and diffusion) for gases as well as mixtures. Classical considerations have been used throughout so that on the basis of this work reliable estimates of transport properties are not possible at such temperatures where quantum mechanical effects may be important. Further, we treat the gas concerned as dilute, so that only binary collisions are important and pairwise additivity rule also holds. The numerical values, therefore, may be regarded as referring to a pressure level of one atmosphere.

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#### THERMAL CONDUCTIVITY OF GASES AND GASEOUS MIXTURES

Saxena and coworkers (23-31) have reported the experimental data as determined from conductivity columns in the temperature range 350-1500°K for monatomic gases: helium, neon, argon, krypton and xenon; homonuclear diatomic gases: hydrogen, deuterium, nitrogen and oxygen; heteronuclear diatomic gas: carbon monoxide; and nonpolar triatomic gases: nitrous oxide and carbon dioxide. The conductivity data on these twelve gases as reported by Saxena and coworkers (23-31) were fitted to linear, quadratic and cubic polynomials in temperature to determine an adequate representation of the raw data. These are

$$k = a_l + b_l T, (1)$$

$$k = a_q + b_q T + c_q T^2, (2)$$

$$k = a_c + b_c T + c_c T^2 + d_c T^3. (3)$$

In these equations k represents the conductivity of the gas in mw cm<sup>-1</sup> K<sup>-1</sup> and T the temperature in degrees Kelvin. The original data (23-31) were adequately represented and smoothed by an equation similar to (2) and hence, we have reproduced in Table 1 the conductivity values for all these gases as obtained by the quadratic relation. Within the precision and over-all uncertainty of the k determination,  $\pm 2\%$ , the data of Table 1 should be regarded as the experimental values and in the rest of this paper these values will be used wherever necessary. In Tables 2, 3 and 4 are recorded the constants of the linear fit  $(a_l \text{ and } b_l)$ , quadratic fit  $(a_q, b_q \text{ and } c_q)$  and cubic fit  $(a_c, b_c, c_c)$  and  $d_c$ , respectively, for the twelve gases. In each case the appropriateness of the fit is represented by expressing the difference between the experimental and calculated k values by average  $(L_1)$ , least square  $(L_2)$  and maximum  $(L_1)$  percentage deviations. These values of  $L_1$ ,  $L_2$  and  $L_1$  are listed in Tables 2 to 4. Nitrous oxide undergoes partial thermal decomposition above 450°C. Consequently, data up to 450°C were fitted in Eqs. (1)-(3) and values given in Table 1 beyond 750°K are extrapolated results. The k data for this gas were, however, taken by Saxena and Gupta (31) up to 900°C and the fits obtained on the basis of these data are also given in Tables 2 to 4. The fits are not very satisfactory; and this is not surprising because although the geometrical configuration allows very little decomposition of the gas (as the area of the hot-wire surface is very small as compared to the cold wall) to take place, yet at the same time the column method gives k at the wire temperature and corresponding to a composition in equilibrium with it. This point will not be further discussed in this paper as the application of the column method to determine thermal conductivity of chemically reacting gases is receiving our current attention, and a lot needs to be done and understood both theoretically and experimentally. In our subsequent analysis of the k data, therefore, we do not consider nitrous oxide gas further.

The temperature variation of k for pure gases is well represented (32) by polynomials in temperature, the degree of the latter depending upon how wide the temperature range is. The wider the temperature range, the larger will be the degree of the polynomial. This point will be further discussed later. However, both in the analysis of experimental measurements (assignment of temperature) and in the intercomparison of data of different workers, values which differ or refer to a temperature range of a couple of degrees need to be reduced to a single temperature. We suggest below a

TABLE 1

Smoothed Thermal Conductivity Values<sup>a</sup> (k) of Gases in mw cm<sup>-1</sup> K<sup>-1</sup> as a Function of Temperature (T) in  ${}^{\circ}$ K

CO <sub>2</sub>	0.2031 0.2405 0.2405 0.3151 0.3522 0.3891 0.4256 0.4619 0.4977 0.5330 0.6020 0.6020 0.6083 0.7003 0.7003 0.7014 0.71616 0.71616 0.71616 0.71616 0.71616 0.71616	0.8966 0.9200 0.9420
$N_2O^b$	0.2073 0.2482 0.2880 0.3267 0.3643 0.4008 0.4363 0.4706 0.5360 0.5571 0.6260 0.6260 0.638 0.638 0.7307 0.7362 0.7362 0.7362 0.7363 0.7362 0.7362 0.7362 0.7363	0.8371 0.8551 0.8720
00	0.2859 0.3166 0.3475 0.3787 0.4101 0.4416 0.5360 0.5360 0.5360 0.5982 0.6289 0.6592 0.6890 0.7184 0.7472 0.8027 0.8027 0.8027	0.9039 0.9267 0.9483
$O_2$	0.3074 0.3381 0.3687 0.3991 0.4295 0.4596 0.5194 0.5194 0.5194 0.6362 0.6074 0.6648 0.6930 0.7209 0.7209 0.7485 0.8025 0.8028	0.9055 0.9301 0.9542
$Z_{\mathbf{z}}$	0.3110 0.3349 0.3828 0.4067 0.4067 0.4784 0.5262 0.5501 0.5740 0.5740 0.6979 0.6978 0.6936 0.7175 0.7414	0.8131 0.8370 0.8610
$\mathbf{D_2}$	1.538 1.665 1.792 1.918 2.045 2.172 2.299 2.425 2.679 2.806 2.933 3.059 3.186 3.313 3.440 3.567 3.693 3.867 3.947 4.074	4.200 4.327 4.454
${ m H_2}$	2.053 2.241 2.427 2.427 2.794 2.976 3.157 3.338 3.698 3.698 3.878 4.059 4.240 4.423 4.606 4.791 4.978 5.166 5.357 5.746	5.945 6.147 6.352
×	0.0682 0.0766 0.0848 0.0927 0.1003 0.1077 0.1150 0.1220 0.1288 0.1355 0.1420 0.1484 0.1547 0.1669 0.1788 0.1669 0.1788	0.2076 0.2134 0.2192
Kr	0.1072 0.1196 0.1318 0.1436 0.1552 0.1664 0.1774 0.2089 0.2190 0.2288 0.2385 0.2480 0.2385 0.2480 0.2573 0.2665 0.2665 0.2665 0.2755 0.2933 0.2000	0.3191 0.3276 0.3361
Ar	0.2048 0.2258 0.2462 0.2659 0.2851 0.3037 0.3392 0.3727 0.3888 0.4044 0.4197 0.4197 0.4490 0.4490 0.4632 0.4632 0.4632 0.4632 0.4632 0.5040 0.5300	0.5427 0.5552 0.5676
Š.	0.5462 0.5997 0.6510 0.7003 0.7476 0.7930 0.8368 0.8790 0.9197 0.9591 0.9973 1.070 1.106 1.1140 1.174 1.241 1.241 1.273 1.339	1.371 1.405 1.438
Gas He	1.704 1.843 1.982 2.121 2.260 2.400 2.539 2.687 2.955 3.093 3.230 3.366 3.366 3.366 3.366 3.366 3.488 4.158 4.158	4.532 4.653 4.771
T G	350 400 450 500 550 600 650 700 750 800 850 900 950 1100 1150 1250 1350	1400 1450 1500

<sup>&</sup>lt;sup>a</sup> Only three significant figures in k values are consistent with the experimental accuracy in conductivity data. Tabulation of four figures is to facilitate

the numerical processing.

<sup>o</sup> Values based on data taken in the temperature range 50-450°C, and consequently data beyond 750°K are not as reliable as the directly observed values.

TABLE 2		
Constants of the Relation $k = a_l + b_l T$ , $k$ in mw cm <sup>-1</sup> K <sup>-1</sup> and	T in	°K

Gas	$a_l$	$b_1 \times 10^3$	$L_1$ a	$L_2$	$L_{\text{I}}$
He	0.7561	0.02733	0.97	1.1	2.1
Ne	0.3028	0.7875	2.0	2.3	4.8
Ar	0.1024	0,3250	2.1	2.4	4.1
Kr	0.04089	0.2040	1.7	2.0	3.5
Xe	0.02500	0.1340	1.8	2.1	4.1
$H_2$	0.7808	0.03651	0.2	0.3	0.6
$\mathbf{D_2}$	0.6505	0.02536	0.3	0.4	0.7
$N_2$	0.1437	0.4782	2.6	3.1	5.5
$O_2$	0.1112	0.5761	0.8	1.0	1.7
CO	0.08072	0.5986	1.0	1.3	3.1
$CO_2$	-0.02527	0.6784	2.2	2.5	4.8
$N_2O$	-0.06045	0.7701	2.9	4.6	11.2 b
$N_2O$	-0.06004	0.7662	0.9	1.0	1.7 °

 $<sup>^</sup>a$   $L_1$ ,  $L_2$  and  $L_1$  are the average, least square and maximum percentage errors between the computed and experimental k values.

TABLE 3  ${\rm Constants~of~the~Relation~}k=a_q+b_qT+c_qT^2,~k~{\rm in~mw~cm^{-1}~K^{-1}~and~}T~{\rm in~}^\circ{\rm K}$ 

Gas	$a_q$	$b_q  imes 10^3$	$-c_q  imes 10^6$	$L_1{}^a$	$L_2$	$L_{\scriptscriptstyle \mathrm{I}}$
He	0.6877	0.02936	0.1276	0.9	1.0	2.2
Ne	0.1797	0.01137	0.2062	0.5	0.6	1.0
Ar	0.05323	0.4656	0.08328	0.2	0.3	0.7
Kr	0.01815	0.2699	0.03948	0.2	0.3	0.9
Xe	0.009521	0.1790	0.02701	0.4	0.4	0.7
$H_2$	0.7897	0.03623	-0.01809	0.2	0.3	0.5
$\mathbf{D_2}$	0.7073	0.02368	-0.1048	0.1	0.2	0.4
$N_2$	0.05100	0.7438	0.1573	0.3	0.3	0.7
$O_2$	0.07979	0.6671	0.05479	0.2	0.2	0.5
CO	0.04324	0.7072	0.06461	0.4	0.6	1.2
$CO_2$	-0.9150	0.8777	0.1214	0.5	0.5	0.9
$N_2O$	-0.1102	0.9513	0.1414	3.1	4.1	9.7 b
N <sub>2</sub> O	-0.1093	0.9809	0.2178	0.2	0.2	0.4 °

 $<sup>^{</sup>a}$   $L_{1}$ ,  $L_{2}$  and  $L_{1}$  are the average, least square and maximum percentage errors between the computed and experimental k values.

<sup>&</sup>lt;sup>b</sup> Fit based on k data in the temperature range 50–900°C.

<sup>°</sup> Fit based on k data in the temperature range 50-450°C.

<sup>&</sup>lt;sup>b</sup> Fit based on k data in the temperature range 50-900°C.

<sup>&</sup>lt;sup>c</sup> Fit based on k data in the temperature range 50-450°C.

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Consta	NTS OF THE R	LELATION $k=$	$= a_c + b_c T + C$		in mw cm	-1 K -1 and	T in °K
Gas	$a_{c}$	$b_c  imes 10^3$	$-C_c \times 10^6$	$d_c  imes 10^9$	$L_1{}^a$	$L_2$	$L_{\scriptscriptstyle  m I}$
Ша	0.7570	0.02622	0.2020	0.1715	0.0	1.0	

Gas	$a_c$	$b_c  imes 10^3$	$-C_c \times 10^6$	$d_c\! imes\!10^9$	$L_1{}^a$	$L_2$	L
Не	0.7578	0.02623	-0.2920	-0.1715	0.9	1.0	2.2
Ne	0.1001	0.01476	0.6331	0.1623	0.2	0.3	0.6
Ar	0.03753	0.5327	0.1680	0.03230	0.1	0.2	0.4
Kr	0.009820	0.3058	0.08515	0.01752	0.2	0.2	0.6
Xe	0.0008668	0.2163	0.07461	0.01828	0.1	0.2	0.4
$H_2$	0.6658	0.04192	0.7701	0.3354	0.1	0.2	0.5
$\mathbf{D_2}$	0.7171	0.02324	-0.1624	-0.02319	0.1	0.2	0.4
$N_2$	0.05681	0.7189	0.1259	-0.01199	0.3	0.3	0.6
$O_2$	0.09156	0.6162	-0.01062	-0.02535	0.1	0.2	0.5
CO	0.08610	0.5216	-0.1730	-0.09171	0.3	0.3	0.6
$CO_2$	-0.05413	0.7123	-0.09456	-0.08449	0.2	0.3	0.6
$N_2O$	0.1033	-0.1817	-1.673	-0.8779	2.6	3.2	6.3 b
$N_2O$	-0.1100	0.9853	0.2269	0.005989	0.2	0.2	0.4 °

<sup>&</sup>lt;sup>a</sup>  $L_1$ ,  $L_2$  and  $L_1$  are the average, least square and maximum percentage errors between the computed and experimental k values.

procedure appropriate for such a situation, our starting point being the theoretical Chapman-Enskog expression for the thermal conductivity of a monatomic gas,  $k^0$ . This is also referred to as the frozen thermal conductivity when polyatomic systems are involved and different chemical reactions (dissociation, ionization, etc.) may also occur. The formula for  $k^0$  is (1)

$$k^{0} = A \frac{\sqrt{T/M}}{\sigma^{2} \Omega^{(2, 2)*}}.$$
 (4)

Here A is a numerical factor whose magnitude depends primarily on the units in which different quantities are represented in Eq. (4). Thus, if  $k^0$  is expressed in mw cm<sup>-1</sup> K<sup>-1</sup>, T in °K,  $\sigma$  in A (10<sup>-8</sup>), then A is equal to 0.8328. M is the molecular weight of the gas and  $\Omega^{(2,2)*}$  is the reduced dimensionless collision integral (2), and its value depends upon the assumed form for the interaction potential between the molecules of the gas. Differentiation of Eq. (4) and its rearrangement give

$$\frac{T}{k^{o}}\frac{dk^{o}}{dT} = \frac{1}{2} - \frac{T^{*}}{\Omega^{(2,2)*}}\frac{d\Omega^{(2,2)*}}{dT^{*}}.$$
 (5)

 $\Omega^{(2,2)*}$  are tabulated in Ref. (2) for a number of different force forms as a function of reduced temperature  $T^*$ . The latter quantity  $T^*$  is equal to  $kT/\varepsilon$  where k is Boltzmann's constant, and  $\varepsilon$  and  $\sigma$  of Eq. (4) are energy and distance parameters, respectively.  $\varepsilon$  and  $\sigma$  are used as normalizing parameters in the potential function and represent, respectively, the depth of the attractive potential well and the distance at which the potential energy of interaction is zero. Instead of  $\sigma$ , sometimes the distance at which the potential energy is minimum ( $\sigma_m$  or  $r_m$ ) is used and, consequently, many

<sup>&</sup>lt;sup>b</sup> Fit based on k data in the temperature range 50-900°C.

<sup>&</sup>lt;sup>c</sup> Fit based on k data in the temperature range 50-450°C.

authors represent  $\sigma$  by  $\sigma_o$  or  $r_o$  and  $\varepsilon$  by  $\varepsilon_o$ . For the two forms of potential energy functions, namely, (a) Lennard-Jones (12-6) for nonpolar gases,

$$\phi(r) = 4\varepsilon_{o} \left[ \left( \frac{\sigma_{o}}{r} \right)^{12} - \left( \frac{\sigma_{o}}{r} \right)^{6} \right], \tag{6}$$

and (b) Stockmayer (12-6-3) for simple polar gases,

$$\phi(r) = 4\varepsilon_{o} \left[ \left( \frac{\sigma_{o}}{r} \right)^{12} - \left( \frac{\sigma_{o}}{r} \right)^{6} + \delta \left( \frac{\sigma_{o}}{r} \right)^{3} \right], \tag{7}$$

where  $\delta$  is an additional parameter, we have computed the derivative of integral which occurs in Eq. (5) based on the extensive tabulations of  $\Omega^{(2,2)*}$  for the potentials of Eqs. (6) and (7) as given by Hirschfelder, Bird and Spotz (33) and Monchick and Mason (34), respectively. These are recorded in Tables 5 and 6.

The above procedure is easily extended to polyatomic gases on the basis of a relatively simple theory of Hirschfelder (35) according to which the conductivity k is expressed in terms of  $k^0$  by

$$k = k^{0}(0.115 + 0.354 C_{p}/R)$$

$$= k^{0}(0.115 + 0.354 \gamma/\gamma - 1),$$
(8)

where R is the gas constant,  $C_p$  the specific heat at constant pressure and  $\gamma$  the ratio of the specific heat at constant pressure to that at constant volume. Thus, in this theory k varies with temperature in the same way as  $k^0$  as long as  $\gamma$  (or  $C_p$ ) is constant.

This procedure is easily extended to mixtures of gases through a representation of the theoretical expression for conductivity  $k_{\text{mix}}$  in a form which is due to Wassiljewa (36), viz.,

$$k_{\text{mix}} = \sum_{i=1}^{n} k_i \left[ 1 + \sum_{\substack{j=1\\j \neq i}}^{n} \phi_{ij}(X_j/X_i) \right]^{-1}.$$
 (9)

Here n represents the number of components in the mixture,  $X_i$  the mole fraction of the i-th component in the mixture, and  $\phi_{ij}$  are constants which depend upon molecular weights, thermal conductivity, knowledge of intermolecular forces etc. Mason and Saxena (37) derived simple expressions for  $\phi_{ij}$  depending on k and M only and for mixtures of both monatomic and polyatomic gases. Since then this form has been studied in more detail for monatomic (38), polyatomic (39) and polar (40) gases and extensive calculations have been performed (41) including multicomponent systems (42). These studies (37-43) also indicated that  $\phi_{ij}$  are very feebly dependent on temperature and composition. For the present work, these approximations are quite valid for the temperature range involved is small and mixture composition may not change at all. The differentiation of Eq. (9) then gives  $(d k_{\text{mix}}/dT)$  in which no new quantities occur except  $(dk_i/dT)$  and which can be easily evaluated either through Eq. (5) or Eq. (8) and using results of Tables 5 and/or 6, depending upon the nature of gases in the mixture.

The thermal conductivity of a multicomponent mixture can indeed be calculated on the basis of Eq. (9) and with  $\phi_{ij}$  determined as reliably as possible. One of the simplest

TABLE 5  ${\rm Values~of~} d\Omega^{(2,\,2)*}/dT^* {\rm ~as~a~Function~of~} T^* {\rm ~for~the~Lennard-Jones~(12-6)~Intermolecular~Potential}$ 

<u> </u>		<u>,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,</u>	
$T^*$	$d\Omega_{22}^{(2,2)*}$	$T^*$	$d\Omega^{(2,2)*}_{22}$
1	$dT^*$	1	$dT^*$
0.300	-4.402	2.600	-0.1186
0.350	-2.752	2.700	-0.1168
0.400	-2.634	2.800	-0.1049
0.450	-2.332	2.900	-0.09355
0.500	-2.120	3.000	-0.09042
0.550	-1.917	3.100	-0.08491
0.600	-1.739	3.200	-0.08000
0.650	-1.570	3,300	-0.07515
0.700	-1.402	3.400	-0.06936
0.750	-1.280	3.500	-0.07020
0.800	-1.159	3.600	-0.06411
0.850	-1.045	3.700	-0.06038
0.900	-0.9583	3.800	-0.05723
0.950	-0.8812	3.900	-0.05567
1.000	-0.7975	4.000	-0.05317
1.050	-0.7285	4.100	-0.04971
1.100	-0.6687	4.200	-0.04790
1.150	-0.6166	4.300	-0.04667
1.200	-0.5845	4.400	-0.04449
1.250	-0.5270	4.500	-0.04235
1.300	-0.4870	4.600	-0.04115
1.350	-0.4644	4.700	-0.03923
1.400	-0.4168	4.800	-0.03868
1.450	-0.3882	4.900	-0.03720
1.500	-0.3695	5.000	-0.03452
1.550	-0.3546	6.000	-0.04318
1.600	-0.3133	7.000	-0.01543
1.650	-0.3100	8.000	-0.01762
1.700	-0.3065	9.000	-0.01479
1.750	-0.2661	10.000	-0.01267
1.800	-0.2484	20.000	-0.007909
1.850	-0.2396	30.000	-0.003699
1.900	-0.2322	40.000	-0.002476
1.950	-0.2155	50.000	-0.001885
2.000	-0.2186	60.000	-0.001533
2.100	-0.1732	70.000	-0.001289
2.200	-0.1746	80.000	-0.001088
2.300	-0.1522	90.000	-0.000983
2.400	-0.1473	100.000	-0.000788
2.500	-0.1285		

TABLE  $\,6\,$  Values of  $d\Omega^{(2,\,2)*}/dT^*$  as a Function of  $\delta$  and  $T^*$  for the Lennard–Jones type (12-6-3) Potential

		· · · · · · · · · · · · · · · · · · ·		
<i>T</i> *	$\delta = 0$	$\delta = 0.25$	$\delta = 0.50$	$\delta = 0.75$
0.1	-13.37	-14.76	-20.25	-29.53
0.2	-5.346	-6.195	-8.136	-10.74
0.3	-3.492	-3.662	-4.237	-5.256
0.4	-2.748	-2.736	-2.946	-3.393
0.5	-2.219	-2.189	-2.241	-2.471
0.6	-1.794	-1.746	-1.772	-1.910
0.7	-1.456	-1.416	-1.439	-1.529
0.8	-1.189	-1.169	-1.174	-1.248
0.9	-0.9783	-0.9612	-0.9729	-1.039
1.0	-0.8158	0.8040	-0.8147	-0.8707
1.2	-0.5802	-0.5752	-0.6002	-0.6524
1.4	-0.4297	-0.4338	-0.4495	-0.4907
1.6	-0.3278	-0.3304	-0.3469	-0.3831
1.8	-0.2573	-0.2565	-0.2770	-0.3027
2.0	-0.2073	-0.2153	-0.2256	-0.2500
2.5	-0.1310	-0.1294	-0.1432	-0.1619
3.0	-0.09092	-0.09478	-0.1004	-0.1108
3.5	-0.06761	-0.06886	-0.07425	-0.08278
4.0	-0.05252	-0.05491	-0.05857	-0.06275
5.0	-0.03566	-0.03578	-0.03805	-0.04280
6.0	-0.02643	-0.02708	-0.02852	-0.03047
7.0	-0.02088	-0.02113	-0.02211	-0.02373
8.0	-0.01721	-0.01749	-0.01811	-0.01923
9.0	-0.01461	-0.01481	-0.01523	-0.01609
10	-0.01268	-0.01271	-0.01311	-0.01367
12	-0.01003	-0.01019	-0.01045	-0.01082
14	-0.008290	-0.008328	-0.008438	-0.008683
16	-0.007062	-0.007075	-0.007207	-0.007370
18	-0.006140	-0.006229	-0.006241	-0.006387
20	-0.005429	-0.005409	-0.005489	-0.005637
25	-0.004199	-0.004227	-0.004254	-0.004245
30	-0.003395	-0.003410	-0.003411	-0.003478
35	-0.002844	-0.002859	-0.002866	-0.002859
40	-0.002421	-0.002376	-0.002405	-0.002549
50	-0.002044	-0.002649	-0.002565	

TABLE 6 (continued)

T*	$\delta = 1.0$	$\delta = 1.5$	$\delta = 2.0$	$\delta = 2.5$
0.1	-37.66	-50.30	-61.59	-70.88
0.2	-13.33	-17.78	-21.51	-24.83
0.3	-6.444	-8.763	-10.73	-12.41
0.4	-4.036	-5.450	-6.671	-7.762
0.5	-2.857	-3.774	-4.630	-5.386
0.6	-2.158	-2.807	-3.422	-3.985
0.7	-1.715	-2.197	-2.668	-3.109
0.8	-1.394	-1.761	-2.142	-2.487
0.9	-1.145	-1.445	-1.736	-2.017
1.0	-0.9803	-1.240	-1.491	-1.731
1.2	-0.7188	-0.8983	-1.084	-1.259
1.4	-0.5492	-0.6998	-0.8473	-0.9826
1.6	-0.4288	-0.5483	-0.6705	-0.7805
1.8	-0.3462	-0.4403	-0.5407	-0.6381
2.0	-0.2863	-0.3720	-0.4615	-0.5359
2.5	-0.1801	-0.2302	-0.2868	-0.3501
3.0	-0.1282	-0.1699	-0.2136	-0.2550
3.5	-0.09450	-0.1210	-0.1532	-0.1877
4.0	-0.07123	-0.09550	-0.1170	-0.1460
5.0	-0.04768	-0.05808	-0.07673	-0.09094
6.0	-0.03362	-0.04301	-0.05161	-0.06456
7.0	-0.02593	-0.03136	-0.03895	-0.04671
8.0	-0.02075	-0.02486	-0.03000	-0.03612
9.0	-0.01713	-0.02013	-0.02412	-0.02871
10	-0.01474	-0.01701	-0.01991	-0.02340
12	-0.01112	-0.01260	-0.01451	-0.01686
14	-0.009136	-0.01005	-0.01131	-0.01275
16	-0.007592	-0.008267	-0.009135	-0.01027
18	-0.006543	-0.006996	-0.007654	-0.008437
20	-0.005700	-0.006051	-0.006596	-0.007131
25	-0.004379	-0.004573	-0.004782	-0.005200
30	-0.003489	-0.003616	-0.003799	-0.003989
35	-0.002911	-0.002990	-0.003075	-0.003269
40	-0.002446	-0.002540	-0.002739	-0.002619
50	-0.002526	-0.002221		0.003730

and fairly reliable procedures consists in the expression derived by Mason and Saxena (37), viz.,

$$\phi_{ij} = \frac{1.065}{2\sqrt{2}} \left( 1 + \frac{M_i}{M_j} \right)^{-\frac{1}{2}} \left[ 1 + \left( \frac{k_i^0}{k_j^0} \right)^{\frac{1}{2}} \left( \frac{M_i}{M_j} \right)^{\frac{1}{2}} \right]^2$$
 (10)

for mixtures of nonpolar gases, and the numerical constant 1.065 is replaced by 0.85 for mixtures of polar-non-polar gases (40). In this calculation one essentially needs the thermal conductivity data for pure gases at the temperature of interest. If thermal conductivity data at one or two compositions are available for related binary

TABLE 7 VALUES OF  $\phi_{12}$  AND  $\phi_{21}$  FOR THE BINARY COMBINATIONS OF RARE GASES

Gas Pair	$\phi_{12}$	$\phi_{21}$
Ar+He	0.3402	2.788
Ar+Ne	0.6209	1.656
Ar+Kr	0.7622	1.458
Ar+Xe	0.3731	2.214
He+Ne	0.3588	2.195
He+Kr	0.4641	2.954
He+Xe	0.3231	3.290
Kr+Xe	0.4596	2.265
Ne+Kr	0.7756	1.294
Ne+Xe	0.3049	2.569

systems, many other choices for evaluating  $\phi_{ij}$  are available. Extensive calculations have been made to assess the relative appropriateness of different alternatives (37–43). It will be very helpful if  $\phi_{ij}$  be tabulated at one temperature for various binary systems and which may be used in conjunction with Eq. (9) for the computation of  $k_{\text{mix}}$ . We have measured thermal conductivity of binary, ternary and quaternary mixtures of gases as a function of temperature and composition using the thick-wire variant of the hot-wire method (44). We have also attempted to discriminate between the different methods for predicting  $k_{\text{mix}}$  and the values of  $\phi_{12}$  and  $\phi_{21}$  which satisfactorily reproduce the critically evaluated observed  $k_{\text{mix}}$  data (32) as a function of temperature and composition. A detailed study for the ten binary systems of rare gases was presented by Saxena (45) and recently he (46) has extended this study to eighty binary systems. As an illustration, the  $\phi_{ii}$  values for the ten rare gas mixtures are listed in Table 7 and the computed  $k_{mix}$  values in Table 8. The latter values refer to equimolar mixtures and the twenty-four temperature levels arbitrarily chosen in the temperature range 350-1500°K. In these calculations the pure conductivity data of Table 1 are used. It may be emphasized that  $\phi_{ij}$  are independent of temperature to a large extent, so that the evaluation of thermal conductivity at high temperatures is primarily and mainly limited by the availability of data on pure gases. In the next section we apply the principle of corresponding states to thermal conductivity data on pure gases and examine to what extent this approach permits the establishment of k data at higher temperatures. This is important, and, as is also well-known (32), very little experimental

TABLE 8

TYPICAL VALUES OF THE THERMAL CONDUCTIVITY (IN MW cm<sup>-1</sup> K<sup>-1</sup>) for the Binary Combinations of Rare Gases <sup>a</sup>

Gas pair	Ar+He	Ar+Ne	Ar+Kr	Ar+Xe	He+Ne	He+Kr	He+Xe	Kr+Xe	Ne+Kr	Ne+Xe
$T$ , ${}^{\circ}$ K	-	-	  - 	-	-	-				
350	0.602	0.348	0.145	0.114	0.939	0.504	0.448	0.0801	0.302	0.208
400	0.655	0.366	0.160	0.126	1.02	0.548	0.487	0.0892	0.330	0.227
450	0.707	0.396	0.175	0.138	1.10	0.591	0.526	0.0982	0.357	0.247
500	0.759	0.426	0.189	0.150	1.18	0.635	0.565	0.107	0.384	0.266
550	0.810	0.455	0.206	0.161	1.26	0.678	0.603	0.116	0.411	0.285
009	0.860	0.483	0.217	0.172	1.33	0.721	0.641	0.124	0.437	0.303
650	0.910	0.511	0.231	0.183	1.41	0.764	0.679	0.132	0.462	0.321
700	096.0	0.538	0.244	0.194	1.48	908.0	0.717	0.141	0.487	0.338
750	1.01	0.565	0.257	0.204	1.56	0.848	0.754	0.149	0.511	0.355
800	1.06	0.590	0.270	0.214	1.63	0.890	0.791	0.157	0.535	0.372
850	1.11	0.615	0.282	0.224	1.70	0.931	0.828	0.164	0.558	0.388
006	1.15	0.640	0.295	0.234	1.77	0.973	0.865	0.172	0.581	0.404
950	1.20	0.664	0.307	0.244	1.84	1.01	0.901	0.179	0.603	0.420
1000	1.25	0.687	0.318	0.253	1.90	1.05	0.937	0.187	0.624	0.435
1050	1.29	0.710	0.330	0.262	1.98	1.09	0.973	0.194	0.645	0.450
1100	1.34	0.732	0.341	0.271	2.05	1.13	1.01	0.201	0.665	0.464
1150	1.39	0.753	0.352	0.280	2.11	1.17	1.04	0.208	0.685	0.478
1200	1.43	0.773	0.362	0.288	2.18	1.21	1.08	0.214	0.705	0.492
1250	1.48	0.793	0.372	0.296	2.24	1.25	1.11	0.221	0.723	0.505
1300	1.52	0.813	0.382	0.304	2.31	1.29	1.15	0.227	0.741	0.518
1350	1.56	0.831	0.392	0.312	2.37	1.33	1.18	0.233	0.759	0.530
1400	1.61	0.849	0.401	0.319	2.43	1.37	1.22	0.239	0.776	0.542
1450	1.65	0.867	0.410	0.327	2.49	1.41	1.25	0.245	0.792	0.553
1500	1.69	0.884	0.419	0.334	2.55	1.44	1.28	0.251	0.808	0.565

<sup>&</sup>lt;sup>a</sup> Computed values refer to arbitrarily chosen temperatures and to equal proportions of the two gases in the mixture.

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data exist at the present time beyond 1500°K and experimental techniques are practically nonexistent for the measurement of transport properties above 2000°K.

## THE PRINCIPLE OF CORRESPONDING STATES AND THERMAL CONDUCTIVITY OF GASES

The principle of corresponding states has been applied to various equilibrium and nonequilibrium properties of gases with great success. The principle is well established and is adequately demonstrated for simple fluids (47, 48). Even for complicated fluids, it has been shown (49, 50) how this principle can be applied in terms of more elaborate relations, generally involving one additional parameter more than for simple fluids. Amongst transport properties, this principle has been extensively studied against data on the viscosity of gases up to high densities (51, 52) as well as for simple liquids (53) and their binary mixtures (54). A more detailed application on the data of viscosity of nonpolar gases at ordinary pressure is attempted by Stiel and Thodos (55). Carswell and Stryland (56) demonstrated the applicability of the principle by analysing the data on the diffusion coefficient of gases. The application of the ideas of corresponding states to thermal conductivity data, in general, requires more caution, because this is the only property unlike the ones mentioned above, which is sensitive to the internal degrees (rotation and vibration) of freedom of the molecules. We shall, consequently, expect departures from the principle of corresponding states for polyatomic molecules and in increasing magnitude with the complexity in molecular structure. We first formulate the form of the law for thermal conductivity of pure gases at ordinary pressure.

According to Eq. (4) a plot of

$$\frac{\sqrt{M}k^0\sigma^2}{\sqrt{\varepsilon}}$$

should be a universal function of  $T^*$ . Application of the principle of corresponding states to conductivity data in this form requires the knowledge of two potential parameters  $\varepsilon$  and  $\sigma$ . As even for rare gases, different workers have reported sufficiently different values of parameters as determined from different properties (2) (primarily viscosity and second virial coefficient), the actual test of the law presents some difficulty. In fact, the observed diversity in the magnitude of these parameters is also a weak indication of the failure of the law. Such considerations as the inadequate functional choice for the central potential function, varying experimental uncertainties involved in the measurement of different properties and also the different degrees of sensitivity of the potential function to different properties etc. can lead to the scatter observed (2) in the values of the potential parameters. An easy way out of this situation is to use critical constants. It has been demonstrated (2, 57) that to a reasonable degree of accuracy the energy parameter  $(\varepsilon/k)$  is a linear function of the critical temperature  $(T_c)$  and  $\sigma^3$  of critical volume  $(V_c)$ . As the measurement of  $V_c$  is difficult, it can be replaced by critical pressure  $P_c$ . This immediately suggests (2), then, that  $k^0 M^{1/2} P_c^{-2/3} T_c^{1/6}$  should be a unique function of  $T/T_c$ . Instead of critical constants, one can choose the boiling point constants; in fact, sometimes the latter approach is preferable. As our correlations are for conditions far removed from the critical state, we will continue to use critical constants which are accurately known for all the gases which possess current interest for us. The critical constants of the ten gases of Table 1 are given in Table 9 and are taken from the compilation of Stiel and Thodos (55). The values of the compressibility factor at critical temperature for these gases as well as the factor  $M^{1/2}P_c^{-2/3}T_c^{1/6}$  are also listed in Table 9.

TABLE 9	
VALUES OF CERTAIN CONSTANTS AND FACTORS F	OR THE PURE GASES

Gas	Molecular weight	Critical temperature (°K)	Critical pressure (atm)	$\frac{P_c V_c}{RT_c}$	$M^{1/2}P_c^{-2/3}T_c^{1/6}$
He	4.003	5.206	2.26	0.306	1.529
Ne	20.183	44.5	26.86	0.307	0.9429
Ar	39.944	151.2	48.00	0.291	1.105
Kr	83.80	209.4	54.18	0.292	1.558
Xe	131.3	289.8	57.64	0.290	1.975
$H_2$	2.016	33.3	12.8	0.305	0.4654
$N_2$	28.02	126.2	33.5	0.291	1.141
$O_2$	32.00	154.8	50.1	0.293	0.9645
CO	28.01	133.0	34.5	0.294	1.128
$CO_2$	44.01	304.2	72.85	0.275	0.9863

In Fig. 1 are plotted the data of Table 1 for Ne, Ar, Kr, Xe,  $H_2$ ,  $N_2$ ,  $O_2$ , CO, and  $CO_2$ . For the sake of convenience, the data for He are plotted in Fig. 2 because of the large values of  $T/T_c$  involved; and to show their relation with the data for other rare gases, the data of neon are also shown. It will be noticed in Fig. 1, that data for the four rare gases approximately lie on a curve. Within this limitation, the law of corresponding states may be regarded as valid to k for rare gases. It will considerably help

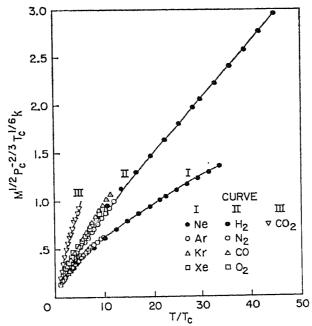


Fig. 1. Plot of  $M^{1/2}P_c^{-2/3}T_c^{1/6}k$  versus  $T/T_c$  for monatomic, diatomic and polyatomic gases. The continuous curves are smooth plots through the points on eye judgement and are not according to the polynomials discussed in the text.

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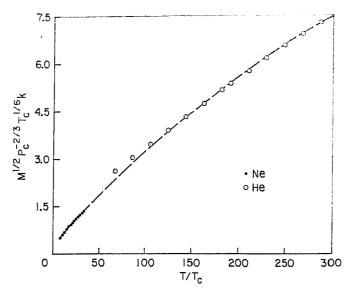


Fig. 2. The legend is same as in Fig. 1 except that the data points refer to the two gases, helium and neon. The dashed curve is again on eye judgement.

if data were available for a still wider temperature range, particularly for neon so that in Fig. 2 we may get a continuous curve instead of a big gap between the points referring to neon and helium. By minimizing the maximum deviation, an eighteen order (i = 19 in Eq. (11)) polynomial adequately fitted the data for rare gases. The constants of the polynomial

$$kM^{1/2}P_c^{-2/3}T_c^{1/6} = \sum_{i=1}^{19} a_i (T/T_c)^{i-1}$$
(11)

referring to the rare gases data of Fig. 1 are

$$a_{1} = -2.950, \ a_{2} = 8.822, \ a_{3} = -11.02, \ a_{4} = 7.969, \ a_{5} = -3.721, \ a_{6} = 1.197, \ a_{7} = -0.2767, \ a_{8} = 0.04721, \ a_{9} = -0.6064 \times 10^{-2}, \ a_{10} = 0.5937 \times 10^{-3}, \ a_{11} = -0.4463 \times 10^{-4}, \ a_{12} = 0.2582 \times 10^{-5}, \ a_{13} = -0.1145 \times 10^{-6}, \ a_{14} = 0.3858 \times 10^{-8}, \ a_{15} = -0.9680 \times 10^{-10}, \ a_{16} = 0.1751 \times 10^{-11}, \ a_{17} = -0.2157 \times 10^{-13}, \ a_{18} = 0.1618 \times 10^{-15}, \ \text{and} \ a_{19} = -0.5575 \times 10^{-18}; \ \text{and similar constants of the polynomial which reproduce the curve of Fig. 2 are} \ a_{1} = 0.3803, \ a_{2} = -0.07562, \ a_{3} = 0.02674, \ a_{4} = -0.3160 \times 10^{-2}, \ a_{5} = 0.2264 \times 10^{-3}, \ a_{6} = -0.1079 \times 10^{-4}, \ a_{7} = 0.3579 \times 10^{-6}, \ a_{8} = -0.8491 \times 10^{-8}, \ a_{9} = 0.1475 \times 10^{-9}, \ a_{10} = -0.1909 \times 10^{-11}, \ a_{11} = 0.1862 \times 10^{-13}, \ a_{12} = -0.1379 \times 10^{-15}, \ a_{13} = 0.7739 \times 10^{-8}, \ a_{14} = -0.3271 \times 10^{-20}, \ a_{15} = 0.1023 \times 10^{-22}, \ a_{16} = -0.2295 \times 10^{-25}, \ a_{17} = 0.3491 \times 10^{-28}, \ a_{18} = -0.3222 \times 10^{-31}, \ \text{and} \ a_{19} = 0.1362 \times 10^{-34}. \$$

These polynomials (constants of Eq. (12) for Ar, Kr and Xe, and constants of Eq. (13) for Ne and He) represent the original data better than the inherent scatter of the data seen in Figs. 1 and 2. To facilitate the use of the correlations developed above we have tabulated in Tables 10 and 11 values of  $kM^{1/2}P_c^{-2/3}T_c^{1/6}$  for round values of  $T/T_c$  as obtained from Eq. (11) employing constants (12) and (13), respectively.

TABLE 10 Values of  $kM^{1/2}P_c^{-2/3}T_c^{1/6}~(\simeq Y)$  as a Function of  $T/T_c~(\simeq X)^a$ 

X	$Y_{ep}$	X	$Y^b$	X	$Y^b$
1.2	0.1246	4.4	0.3704	11	0.6594
1.3	0.1417	4.6	0.3824	12	0.6860
1.4	0.1540	4.8	0.3945	13	0.7189
1.5	0.1633	5.0	0.4064	14	0.7651
1.6	0.1709	5.2	0.4180	15	0.8158
1.7	0.1779	5.4	0.4294	16	0.8552
1.8	0.1846	5.6	0.4402	17	0.8784
1.9	0.1915	5.8	0.4505	18	0.8975
2.0	0.1988	6.0	0.4601	19	0.9281
2,2	0.2143	6.2	0.4691	20	0.9705
2.4	0.2310	6.4	0.4775	21	1.008
2.6	0.2480	6,6	0.4855	22	1.029
2.8	0.2646	6.8	0.4930	23	1.043
3.0	0.2803	7.0	0.5003	24	1.076
3.2	0.2951	7.5	0.5183	25	1.131
3.4	0.3089	8.0	0.5374	26	1.169
3.6	0.3218	8.5	0.5586	27	1.161
3.8	0.3343	9.0	0.5813	28	1.156
4.0	0.3464	9.5	0.6042	29	1 224
4.2	0.3584	10	0.6255	30	1.229

TABLE 11 Values of  $kM^{1/2}P_{\rm c}^{-2/3}T_{\rm c}^{1/6}$  ( $\simeq Y$ ) as a Function of  $T/T_{\rm c}$  ( $\simeq X$ ) $^a$ 

X	$Y^b$	X	$Y^b$	X	$Y^b$
8.0	0.5207	26	1.143	65	2.537
8,5	0.5432	28	1.198	70	2.682
9.0	0.5654	30	1.253	75	2.801
9.5	0.5874	32	1.308	80	2.903
10.0	0.6089	34	1.364	85	3.001
10.5	0.6301	36	1.424	90	3.102
11.0	0.6508	38	1.486	95	3.211
11.5	0.6712	40	1.553	100	3.325
12.0	0.6911	42	1.624	110	3.558
12.5	0.7107	44	1.700	120	3.777
13.0	0.7299	46	1.779	130	3.991
14.0	0.7672	48	1.862	140	4.214
15.0	0.8032	50	1.946	150	4.441
16.0	0.8380	52	2.032	160	4.659
17.0	0.8719	54	2.118	170	4.871
18.0	0.9048	56	2.202	180	5.092
19.0	0.9369	58	2,283	190	5.309
20.0	0.9682	60	2.361	210	5.728
22.0	1.029	62	2.435	230	6.161
24.0	1.087	64	2.504	250	6.594

<sup>&</sup>lt;sup>4</sup> According to Eqs. (11) and (12). <sup>5</sup> Here k,  $P_c$  and  $T_c$  are in mW cm<sup>-1</sup> K<sup>-1</sup>, atm, and <sup>6</sup>K, respectively.

<sup>&</sup>lt;sup>a</sup> According to Eqs. (11) and (13). <sup>b</sup> Here k,  $P_c$  and  $T_c$  are in mW cm<sup>-1</sup> K<sup>-1</sup>, atm, and °K, respectively.

The data for diatomic gases in Fig. 1 represent a larger scatter than found for monatomic gases. It is clear from Eq. (8) that the curve for diatomic gases will be different from that for monatomic gases. However, if we hold (35) that the assumption of local chemical equilibrium, i.e., no relaxation for internal-translational energy exchange, is valid, and the transport of internal energy is characterized by a diffusion process, the latter having the same value as the mass diffusion coefficient, it is reasonable to assume that in Fig. 1 the data for all diatomic gases will cluster along a uniform curve, following and in accordance with the principle of corresponding states. At even moderate temperatures the assumption I stated above is found to be invalidated (58-60) to some extent and relaxation plays an increasing role with the rise in the temperature of the gas. It is not quite clear at the present time how serious the second assumption for such simple molecules is and whether most of the available k data can be correlated on the basis of thermal conductivity theories (59-61) which account for the relaxing nature of the internal energy only. We, thus, have qualitative explanations for the data of diatomic gases in Fig. 1 to lie on a curve different from that for monatomic gases. Also, the scatter in the data is to be expected because of the two major limitations (mentioned above) inherent in Eq. (8). It is reasonable to conclude, therefore, that the principle of corresponding states will be applicable to diatomic gases in a more complicated fashion than for monatomic gases and may involve additional parameter or parameters. The development of such a law will have to await simultaneous progress in our theoretical understanding concerning the assumptions mentioned above and the experimental techniques to determine accurately the thermal conductivity of gases at higher temperatures, i.e., greater than about 1500°K.

The points corresponding to carbon dioxide in Fig. 1 again lie on a curve different from that for monatomic or diatomic gases. This does not necessarily evade the prediction of the principle of corresponding states; rather, it confirms the views expressed above in connection with the diatomic gases. In fact the k data for carbon dioxide could not be explained (30) on the basis of either Eq. (8) or more complicated theories (59, 61), and it is concluded (30) that the second assumption mentioned above is seriously in error for this gas. Fortunately, experiments using laser beams have been performed (62) which show a smaller value for the diffusion coefficient characterizing the transport of internal energy than the mass diffusion coefficient. This is additional evidence favoring the need of a more complicated principle describing the application of the principle of corresponding states to thermal conductivity data for polyatomic molecules.

In conclusion, unlike viscosity (55), more complicated versions will have to be developed to express the corresponding state principle for polyatomic fluids. This is in complete accordance with what has been done (49, 50) even for the equilibrium properties of gases of complicated molecular structure. Thodos and coworkers (63) have applied dimensional analysis arguments to develop correlations useful for predicting k values. In the opinion of this author it is still premature to assess the useful controlling parameters, and it is hoped that our understanding before long will advance to a point when a successful corresponding states treatment appropriate for polyatomic fluids will be possible to develop. We, however, do recommend the results of Tables 10 and 11 to be used for the prediction of thermal conductivity of monatomic gases at high temperatures, till either more reliable experimental data or theoretical

techniques become available as a better alternative. Indeed, with the availability of pure gas conductivity data at higher temperatures the techniques pointed out for the computation of multicomponent mixture conductivity in the previous section, may be used to generate values for mixtures of interest.

## VISCOSITY AND DIFFUSION COEFFICIENTS OF GASES AND GASEOUS MIXTURES

The availability of thermal conductivity data as a function of temperature provides a reliable base, within the framework of kinetic theory, to compute viscosities of gases and gaseous mixtures. Such principles and procedures have been described and tested in a number of instances so that only a brief review is given here.

The theory (1, 2) of monatomic gases provides a simple relation between  $k^0$  and  $\eta$ , so that the computation of  $\eta$  is a straightforward job once  $k^0$  values are known. For polyatomic gases, in addition, Eq. (8) may be used to calculate  $\eta$ .

The calculation of viscosity for multicomponent gas mixtures  $\eta_{mix}$  is somewhat similar to that described above for  $k_{\rm mix}$ . For example, Wilke (64) quite some time back suggested an equation similar to (9), and many other procedures have been suggested to evaluate the Sutherland coefficients (65)  $\psi_{ij}$  similar to  $\phi_{ij}$  in Eq. (9). Gambhir and Saxena (38) examined the temperature and composition dependencies of  $\psi_{ij}$  on the basis of rigorous kinetic theory expression for  $\eta_{\rm mix}$  and found these to be quite weak. They (38, 65) found that simple relations connect  $\psi_{ij}$  with  $\psi_{ji}$ . Extensive calculations have been performed to check out these procedures and many more of somewhat similar nature and scope including nonpolar and polar gases (65-70).

It is interesting to point out that the conductivity data of Table 1 have been used by Saxena and Saxena (26) to generate  $\eta$  for argon in the temperature range 300-1500°K. This provides an opportunity to assess the potential behind the procedures outlined above up to such high temperatures for the first time. Comparison of the directly measured (71) values with the indirectly generated values (26) revealed that the two sets differ by 0.06, 0.16, 0.86, 1.4, 1.4 and 0.5% at 500, 700, 900, 1100, 1300 and 1500°K, respectively. The overall average absolute deviation being 0.7% while the estimated probable uncertainty of the experimental viscosity data (71) is  $\pm 1 \%$ . Indeed this is a very favorable check and confirms the high reliability associated with the calculation procedures described above.

Calculation of self-diffusion  $D_{ii}$  or mutual diffusion  $D_{ij}$  coefficients is again possible on the basis of kinetic theory (1, 2) and working relations between thermal conductivity and diffusion coefficients are summarized by Gandhi and Saxena (72) for monatomic gases and by Mathur and Saxena (73) for polyatomic gases.

The accuracy of the interrelation between  $\eta_{mix}$  and  $k_{mix}$  was demonstrated by Saxena and Agrawal (74), while that of viscosity and diffusion coefficients by Saxena and Narayanan (75). Weissman and Mason (76) have used the reverse procedure and computed the diffusion coefficients from the available viscosity data for nonpolar (76), polar (77) gases including atoms (78). Since then, this procedure is used more or less as a routine to get diffusion coefficients from viscosity and thermal conductivity measurements (79-82).

On the basis of semitheoretical analysis, Gupta and Saxena (83) proposed a simple formula for the calculation of  $D_{ij}$  from  $\eta$  (or k) and  $\phi_{ij}$ . Weissman (84) has also presented a similarly interesting study. It may be pointed out, in conclusion, that as the accuracy of the calculation of  $D_{ij}$  according to different methods (85, 86) is not very good and direct measurements are scarce, the procedures outlined above constitute a potential source for obtaining such information.

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