

ences that any other comparison procedure would not alter the preceding statement. By way of suggesting future lines of attack, it is worth pointing out the similarity between Kozlenkov's relation (14) and a very similar expression underlying the intensity of x-ray scattering by disordered alloys. It can be shown that when short-range order only is present, the intensity

$$I \propto \sum_i \alpha_i \frac{\sin kr_i}{kr_i}, \quad (15)$$

where  $\alpha_i$  is a coefficient dependent on the scattering

power and number of atoms in the  $i$ th shell about a central atom and  $k = (2\pi/\lambda) 2 \sin \theta$ . The close relation between absorption and diffraction has already been pointed out above and suggests that a consideration of the ejected electron's diffraction by the atomic arrays may lead to a more convenient formulation of the absorption process. If successful, such an approach also would have the advantage of making absorption-edge studies amenable to the investigation of the structure of solids. A more rigorous theory, however, doubtlessly also will require more exact experimental measurements than are generally available at the present time.

## Thermal Conductivity of Multicomponent Mixtures of Inert Gases

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### I. INTRODUCTION

THE proper understanding of the process of thermal conduction in monatomic gases is not only important in itself but is also basic for the more complicated case of polyatomic gases. The investigations during the last five years have thrown considerable light on this problem. In this paper we discuss all the experimental and theoretical work with a view to get an over-all assessment.

Three different groups of workers have reported the experimental thermal conductivity data of binary and ternary mixtures of inert gases. These are: (a) Saxena (1956, 1957) and Srivastava and Saxena (1957a, 1957b), who determined the thermal conductivity of six binary gas systems and of two ternary gas systems at 38°C as a function of composition; (b) von Ubisch (1959), who measured the thermal conductivity of all the ten possible binary systems of the five stable inert gases, and of the ternary system He-Kr-Xe for different proportions of the constituents at 29° and 520°C; and (c) Thornton (1960, 1961) who reported on the thermal conductivity of seven binary gas pairs at 18°C and again as a function of composition.

The *rigorous* treatment of the phenomenon of thermal conduction in gases was given by Enskog

(1911) and Chapman (1917) and is adequately described by Chapman and Cowling (1952), and Hirschfelder, Curtiss, and Bird (1954). Recently Muckenfuss and Curtiss (1958) have derived an equation for the complete second approximation to the thermal conductivity of multicomponent gas mixtures. Mason (1958) gave a somewhat simpler expression and Mason and Saxena (1959) have investigated the relative accuracies of both these formulations. Muckenfuss' and Curtiss' (1958) formula for the thermal conductivity of an  $n$ -component mixture can be written after the modification suggested by Mason and Saxena (1959) in the following form:

$$\lambda_{\text{mix}} = \frac{\begin{vmatrix} L_{11} & \cdots & L_{1n} & x_1 \\ \vdots & & \vdots & \vdots \\ L_{n1} & \cdots & L_{nn} & x_n \\ x_1 & \cdots & x_n & 0 \end{vmatrix}}{\begin{vmatrix} L_{11} & \cdots & L_{1n} \\ \vdots & & \vdots \\ L_{n1} & \cdots & L_{nn} \end{vmatrix}}, \quad (1)$$

where

$$L_{ii} = -\frac{4x_i^2}{[\lambda_i]_1} - \frac{16T}{25p} \sum_{\substack{k=1 \\ k \neq i}}^n \frac{x_i x_k \left[ \frac{15}{2} M_i^2 + \frac{5}{2} M_k^2 + 4M_i M_k A_{ik}^* \right]}{(M_i + M_k)^2 D_{ik}}, \quad (2)$$

$$L_{ij} \ (i \neq j) = \frac{16T x_i x_j M_i M_j (10 - 4A_{ij}^*)}{(M_i + M_j)^2 D_{ij}}. \quad (3)$$

Here  $[\lambda_i]_1$  is the first approximation to the thermal conductivity of pure component  $i$  in units of  $\text{erg cm}^{-1} \text{sec}^{-1} \text{deg}^{-1}$ ,  $p$  is the pressure in  $\text{dyne cm}^{-2}$ ,  $x_i$  is the mole fraction of the  $i$ th component,  $D_{ik}$  is the accurate value of the binary diffusion coefficient for components  $i$  and  $k$  in units of  $\text{cm}^2 \text{sec}^{-1}$ , the  $M$ 's are molecular weights, and the  $A_{ik}^*$  are dimensionless ratios of collision integrals [Hirschfelder *et al.* (1954)]. The  $A_{ik}^*$  depend weakly on the temperature and on the force law between molecules  $i$  and  $k$ , and are usually nearly equal to unity.

As earlier pointed out by Mason and Saxena (1958) the calculation of  $\lambda_{\text{mix}}$  according to Eq. (1) has two disadvantages from practical viewpoint. Firstly the formula is quite complicated and involves laborious computation. Secondly a reliable knowledge of force laws for the various molecular interactions involved is essential, which is very seldom available. To get over these difficulties Mason and Saxena (1958) suggested the following *approximate* formula:

$$\lambda_{\text{mix}} = \sum_{i=1}^n \lambda_i \left[ 1 + \sum_{\substack{k=1 \\ k \neq i}}^n G_{ik} \frac{x_k}{x_i} \right]^{-1}, \quad (4)$$

where

$$G_{ik} = \frac{1.065}{2\sqrt{2}} \left( 1 + \frac{M_i}{M_k} \right)^{\frac{1}{2}} \left[ 1 + \left( \frac{\lambda_i}{\lambda_k} \right)^{\frac{1}{2}} \left( \frac{M_i}{M_k} \right)^{\frac{1}{4}} \right]^2. \quad (5)$$

The numerical factor 1.065 in Eq. (5) is introduced to compensate partially for the neglect of higher terms in the expansion of the determinant, Eq. (1), and also to replace a complicated factor in the very first term whose value is close to unity. In assigning this numerical value the data of Srivastava and Saxena (1957b) and Saxena (1957) on the binary gas mixtures were used.

The form of Eq. (4) for  $\lambda_{\text{mix}}$  is not very new, it was suggested long back by Wassiljewa (1904). Lindsay and Bromley (1950) have given the following expression for  $G_{ik}$

$$G_{ik} = \frac{1}{4} \left[ 1 + \left\{ \frac{\eta_i}{\eta_k} \left( \frac{M_k}{M_i} \right)^{\frac{3}{4}} \frac{1 + S_i/T}{1 + S_k/T} \right\}^{\frac{1}{2}} \right]^2 \frac{1 + S_{ik}/T}{1 + S_i/T}, \quad (6)$$

where  $\eta_i$ ,  $\eta_k$  and  $S_i$ ,  $S_k$  are the viscosities and Sutherland constants of the two components, respectively.  $S_{ik}$  is assumed to be the geometric mean of  $S_i$  and  $S_k$ .  $G_{ki}$  is obtained from  $G_{ik}$  by interchanging the subscripts. However, as shown by Srivastava and Saxena (1957b) and Saxena (1957), Eq. (4) in conjunction with Eq. (6) does not yield accurate values for  $\lambda_{\text{mix}}$  and is therefore not considered in this paper.

A modification of the Eq. (4) was therefore also suggested by Srivastava and Saxena (1957b) which involves an additional unknown constant to be determined from the known  $\lambda_{\text{mix}}$  value at one composition. Further,  $G_{ik}$  may be treated as disposable parameters and determined directly from the known experimental  $\lambda_{\text{mix}}$  values at two compositions. These empirically determined  $G_{ik}$  and  $G_{ki}$  are fairly successful in reproducing the experimental data in the entire composition range as well as in predicting the multi-component thermal conductivity. We also consider this *empirical* method of calculating  $\lambda_{\text{mix}}$  in this paper.

In the empirical method of calculating  $\lambda_{\text{mix}}$  a knowledge of its value at two compositions is essential to enable the determination of  $G_{ik}$  and  $G_{ki}$ . If, however, a relation is established between  $G_{ik}$  and  $G_{ki}$  the knowledge of  $\lambda_{\text{mix}}$  at only one composition will be sufficient to determine these two constants. An approximate relation of this type is suggested by the work of Mason and Saxena (1958), *viz.*,

$$G_{ik}/G_{ki} = \lambda_i/\lambda_k. \quad (7)$$

Mason and von Ubisch (1960) have exploited this relation and they write these two constants in the form

$$G_{ik} = \lambda_i/\Lambda_{ik}, \quad G_{ki} = \lambda_k/\Lambda_{ki}, \quad (8)$$

where  $\Lambda_{ik} = \Lambda_{ki}$  is an empirical parameter to be determined from the known thermal conductivity of the binary mixture at one composition. A relation of the type of Eq. (8) is implied in Eq. (7). Mason and von Ubisch (1960) suggested Eqs. (4) and (8) for calculating  $\lambda_{\text{mix}}$  and designate this method of computation as *semiempirical*.

We thus consider in detail four different procedures of calculating  $\lambda_{\text{mix}}$  in this paper. These are, (1) rigorous, Eqs. (1) to (3); (2) approximate, Eqs. (4) and (5); (3) empirical, Eq. (4) along with  $\lambda_{\text{mix}}$  values at two compositions; and (4) semiempirical, Eqs. (4), (8), and  $\lambda_{\text{mix}}$  value at one composition.

## II. COMPARISON OF EXPERIMENT AND THEORY

Calculations described in this section are performed according to the modified exp-six potential [Mason (1954)]

$$\phi(r) = \frac{\epsilon}{1 - \frac{6}{\alpha}} \left[ \frac{6}{\alpha} \exp \alpha \left( 1 - \frac{r}{r_m} \right) - \left( \frac{r_m}{r} \right)^6 \right], \quad (9)$$

where  $\phi(r)$  is the intermolecular potential energy between two molecules at a molecular separation

distance  $r$ ,  $\epsilon$  is the depth of the potential energy minimum,  $r_m$  is the value of  $r$  for which  $\phi(r)$  is a minimum, and  $\alpha$  is a parameter which is measure of the steepness of repulsive potential energy.  $\alpha$ ,  $\epsilon$ , and  $r_m$  are called the potential parameters and the values used in the calculations of this paper are those recorded in Table I.

TABLE I. Exp-six potential parameters.<sup>a</sup>

| Parameter          | Gas | He    | Ne    | Ar    | Kr    | Xe    |
|--------------------|-----|-------|-------|-------|-------|-------|
| $\alpha$           | He  | 12.4  | 13.46 | 13.21 | 12.92 | 12.55 |
|                    | Ne  |       | 14.5  | 14.17 | 13.85 | 13.45 |
|                    | Ar  |       |       | 14.0  | 13.74 | 13.44 |
|                    | Kr  |       |       |       | 13.50 | 13.22 |
|                    | Xe  |       |       |       |       | 13.00 |
| $\epsilon/k$<br>°K | He  | 9.16  | 18.71 | 33.4  | 45.6  | 52.3  |
|                    | Ne  |       | 38.0  | 73.7  | 115.4 | 121.8 |
|                    | Ar  |       |       | 123.2 | 159.2 | 178.5 |
|                    | Kr  |       |       |       | 200.0 | 226.3 |
|                    | Xe  |       |       |       |       | 231.2 |
| $r_m$<br>Å         | He  | 3.135 | 3.143 | 3.488 | 3.539 | 3.65  |
|                    | Ne  |       | 3.147 | 3.443 | 3.484 | 3.574 |
|                    | Ar  |       |       | 3.866 | 3.946 | 4.108 |
|                    | Kr  |       |       |       | 4.036 | 4.221 |
|                    | Xe  |       |       |       |       | 4.45  |

<sup>a</sup> Mason (1955, 1960). Mason and von Ubisch (1960).

In Table II are recorded the experimental [Thornton (1960), (1961)] and computed values of thermal conductivity according to the four different procedures mentioned in the previous section for seven binary systems as a function of composition at 18°C. Experimental  $\lambda_{\text{mix}}$  values of Srivastava and Saxena (1957b) and Saxena (1957) at 38°C as a function of composition are recorded in Table III along with the four sets of calculated values. Similar computed and experimental  $\lambda_{\text{mix}}$  values of von Ubisch (1959) at 29°C are listed in Table IV while at 520°C in Table V.

Some of the computed values of these tables have been reported earlier. Thornton (1960, 1961) gave the rigorous computed values of the mixtures of Table II based on the Lennard-Jones (12-6) intermolecular potential. These values do not differ significantly from those of Table II. The average deviation between the two sets of values for a system never exceeds 1.9% and the average deviation for all the seven systems is only 0.13%. Thus, the use of the correct expression for  $\lambda_{\text{mix}}$  in conjunction with the exp-six potential does not produce any appreciable change in the values over those obtained from the older less accurate expression [Hirschfelder *et al.* (1954).] in conjunction with the Lennard-Jones (12-6) potential. The rigorous values of  $\lambda_{\text{mix}}$  for

mixtures of Table III have also been reported earlier [Saxena (1957), Srivastava and Saxena (1957b)]. Approximate calculations have also been performed by Mason and Saxena (1958), who also presented a graphical comparison with the experimental values. Approximate values reported in Table III were, however, calculated afresh. Rigorous, approximate, and semiempirical calculated values of  $\lambda_{\text{mix}}$  of Tables IV and V are due to Mason and von Ubisch (1960). Approximate calculations, however, have been repeated and only these values are recorded. Some measurements of  $\lambda_{\text{mix}}$  are also available for the ternary mixtures of inert gasses. In Table VI are reported the experimental data of Srivastava and Saxena (1957a) and Saxena (1956) for He-Ar-Xe and Ne-Ar-Kr mixtures at 38°C. Rigorous calculated values of  $\lambda_{\text{mix}}$  are those of Muckenfuss and Curtiss (1958) according to the Lennard-Jones (12-6) potential. Approximate  $\lambda_{\text{mix}}$  values for these mixtures have been reported earlier by Mason and Saxena (1958). In Tables VII and VIII are given the experimental [von Ubisch (1959)] and various calculated values for the He-Kr-Xe mixtures at 29 and 520°C, respectively. The rigorous, approximate and semi-empirical calculated values of  $\lambda_{\text{mix}}$  are those of Mason and von Ubisch (1960). In Tables VI, VII, and VIII,  $X_1$ ,  $X_2$ , and  $X_3$  represent, respectively, the mole fractions of the three molecular species in order of their decreasing molecular weights.

In Table IX are listed the various values of  $G_{ik}$  and  $G_{ki}$  for the three sets of data and according to approximate, empirical, and semi-empirical procedures of calculations. The empirical values of  $G_{ik}$  and  $G_{ki}$  do not exhibit any systematic trend for the same mixture as a function of temperature or at the same temperature from one mixture to another. The empirical values also differ considerably from the semi-empirical and approximate values. The reason for the absence of any such correlating formula in the values of  $G_{ik}$  and  $G_{ki}$  lies in the success of the form of Eq. (4) in reproducing the composition dependence of  $\lambda_{\text{mix}}$  with considerable flexibility in the values of these constants. In fact the different choices of  $\lambda_{\text{mix}}$  for evaluating these two constants yield, in certain cases, widely different coupled values which are equally good in reproducing the composition variation of  $\lambda_{\text{mix}}$ . Recently Gray and Wright (1961) have made a detailed study regarding the nature of these constants. Cowling (1962) interprets  $G_{ik}$  as the measure of the ratio of the efficiencies with which molecules  $k$  and  $i$  separately impede the transport of energy by molecules  $i$ . Gray and Wright (1961, 1962), while interpreting experi-

TABLE II. Various calculated and experimental (Thornton) thermal conductivity values at 18°C. The units of  $\lambda$  are cal cm<sup>-1</sup> sec<sup>-1</sup> deg<sup>-1</sup>.

| Gas pair | $X_1$ | Exptl. | Rigor. | % Dev. | Approx. | % Dev. | Empir. | % Dev. | Semi-empir. | % Dev. |
|----------|-------|--------|--------|--------|---------|--------|--------|--------|-------------|--------|
| He-Xe    | 0.000 | 3560   | 3606   | +1.3   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.063 | 2708   | 2961   | +9.4   | 2890    | +6.7   | 2869   | +5.9   | 2911        | +7.5   |
|          | 0.139 | 2180   | 2378   | +9.1   | 2294    | +5.2   | 2265   | +3.9   | 2324        | +6.6   |
|          | 0.201 | 1800   | 2008   | +11.6  | 1922    | +6.7   | 1894   | +5.2   | 1955        | +8.6   |
|          | 0.304 | 1440   | 1534   | +6.5   | 1455    | +1.0   | 1429   | -0.8   | 1486        | +3.2   |
|          | 0.401 | 1110   | 1196   | +7.8   | 1128    | +1.6   | ...    | ...    | 1154        | +4.0   |
|          | 0.494 | 905    | 940    | +3.9   | 833     | -2.4   | 865    | -4.4   | ...         | ...    |
|          | 0.594 | 680    | 710    | +4.4   | 675     | -0.7   | 659    | -3.1   | 689         | +1.3   |
|          | 0.687 | 518    | 546    | +5.4   | 512     | -1.2   | 502    | -3.2   | 524         | +1.2   |
|          | 0.792 | 356    | 384    | +7.9   | 363     | +2.0   | ...    | ...    | 370         | +3.9   |
|          | 0.898 | 232    | 247    | +6.5   | 235     | +1.3   | 232    | 0.0    | 239         | +3.0   |
|          | 1.000 | 132    | 135    | +2.3   | ...     | ...    | ...    | ...    | ...         | ...    |
| Ne-Xe    | 0.000 | 1160   | 1141   | -1.6   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.103 | 925    | 884    | -4.4   | 908     | -1.8   | ...    | ...    | 909         | -1.7   |
|          | 0.199 | 752    | 711    | -5.5   | 735     | -2.4   | 754    | +0.3   | 737         | -2.0   |
|          | 0.285 | 624    | 591    | -5.3   | 614     | -1.6   | 630    | +1.0   | 616         | -1.3   |
|          | 0.393 | 500    | 473    | -5.4   | 495     | -1.0   | 504    | +0.8   | 496         | -0.8   |
|          | 0.504 | 398    | 379    | -4.8   | 396     | -0.5   | 400    | +0.5   | ...         | ...    |
|          | 0.594 | 327    | 317    | -3.1   | 331     | +1.2   | 330    | +0.9   | 333         | +1.8   |
|          | 0.673 | 277    | 269    | -2.9   | 282     | +2.2   | 279    | +0.7   | 283         | +2.2   |
|          | 0.794 | 213    | 212    | -0.5   | 218     | +2.3   | ...    | ...    | 219         | +2.8   |
|          | 0.903 | 166    | 168    | +1.2   | 169     | +1.8   | 166    | 0.0    | 170         | +2.4   |
| Ar-Xe    | 0.000 | 416    | 412    | -1.0   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.109 | 358    | 361    | +0.8   | 366     | +2.2   | 358    | 0.0    | 360         | +0.6   |
|          | 0.213 | 311    | 319    | +2.6   | 325     | +4.5   | 312    | -0.3   | 315         | +1.3   |
|          | 0.300 | 280    | 289    | +3.2   | 294     | +5.0   | ...    | ...    | 284         | +1.4   |
|          | 0.405 | 251    | 257    | +2.4   | 261     | +4.0   | 247    | -1.6   | 251         | 0.0    |
|          | 0.498 | 226    | 239    | +5.8   | 235     | +4.0   | 223    | -1.3   | ...         | ...    |
|          | 0.598 | 202    | 208    | +3.0   | 210     | +4.0   | 199    | -1.5   | 202         | 0.0    |
|          | 0.701 | 180    | 186    | +3.3   | 177     | -1.7   | 179    | -0.6   | 181         | +0.6   |
|          | 0.792 | 163    | 169    | +3.7   | 169     | +3.7   | ...    | ...    | 164         | +0.6   |
|          | 0.905 | 145    | 149    | +2.8   | 148     | +2.1   | 145    | 0.0    | 146         | +0.7   |
| Kr-Xe    | 0.000 | 220    | 218    | -0.9   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.115 | 207    | 205    | -1.0   | 205     | -1.0   | 207    | 0.0    | 206         | -0.5   |
|          | 0.201 | 197    | 196    | -0.5   | 195     | -1.0   | ...    | ...    | 196         | -0.5   |
|          | 0.296 | 187    | 186    | -0.5   | 185     | -1.1   | 187    | 0.0    | 186         | -0.5   |
|          | 0.397 | 178    | 177    | -0.6   | 175     | -1.7   | 177    | -0.6   | 177         | -0.6   |
|          | 0.491 | 168    | 169    | +0.6   | 166     | -1.2   | 168    | 0.0    | ...         | ...    |
|          | 0.595 | 160    | 161    | +0.6   | 158     | -1.3   | 159    | -0.6   | 160         | 0.0    |
|          | 0.693 | 152    | 154    | +1.3   | 151     | -0.7   | 152    | 0.0    | 152         | 0.0    |
|          | 0.786 | 145    | 147    | +1.4   | 145     | 0.0    | ...    | ...    | 146         | +0.7   |
|          | 0.896 | 138    | 141    | +2.2   | 138     | 0.0    | 138    | 0.0    | 138         | 0.0    |
|          | He-Kr | 0.069  | 3050   | 2971   | -2.6    | 2942   | -3.5   | 2995   | -1.5        | 2952   |
| 0.151    |       | 2500   | 2399   | -4.0   | 2414    | -3.4   | 2457   | -1.7   | 2394        | -4.2   |
| 0.272    |       | 1850   | 1762   | -4.8   | 1809    | -2.2   | ...    | ...    | 1788        | -3.4   |
| 0.353    |       | 1530   | 1474   | -3.7   | 1498    | -2.1   | 1532   | +0.1   | 1479        | -3.3   |
| 0.439    |       | 1210   | 1204   | -0.5   | 1228    | +1.5   | 1251   | +3.4   | ...         | ...    |
| 0.600    |       | 825    | 815    | -1.2   | 833     | +1.0   | 840    | +1.8   | 821         | -0.5   |
| 0.698    |       | 642    | 631    | -1.7   | 645     | +0.5   | 645    | +0.5   | 636         | -0.9   |
| 0.797    |       | 480    | 474    | -1.3   | 484     | +0.8   | ...    | ...    | 478         | -0.4   |
| 0.891    |       | 343    | 346    | +0.9   | 342     | +0.3   | 348    | +1.5   | 349         | +1.7   |
| Ne-Kr    |       | 0.065  | 1030   | 1011   | -1.8    | 1030   | 0.0    | 1034   | +0.4        | 1032   |
|          | 0.111 | 960    | 931    | -3.0   | 950     | -1.0   | 955    | -0.5   | 953         | -0.7   |
|          | 0.229 | 780    | 758    | -2.8   | 778     | -0.3   | ...    | ...    | 782         | +0.3   |
|          | 0.339 | 650    | 635    | -2.3   | 651     | -0.2   | 648    | -0.3   | 655         | +0.8   |
|          | 0.438 | 568    | 542    | -4.6   | 556     | +2.1   | 559    | -1.6   | 560         | -1.4   |
|          | 0.533 | 482    | 467    | -3.1   | 479     | +0.6   | 470    | -2.5   | ...         | ...    |
|          | 0.647 | 400    | 390    | -2.5   | 400     | +0.0   | 390    | -2.5   | 402         | +0.5   |
|          | 0.797 | 305    | 307    | +0.7   | 310     | +1.6   | ...    | ...    | 315         | +3.3   |
|          | 0.889 | 257    | 264    | +2.7   | 269     | +4.7   | 263    | +2.3   | 269         | +4.7   |
| Ar-Kr    | 0.109 | 387    | 381    | -1.6   | 385     | -0.5   | 387    | 0.0    | 379         | -2.1   |
|          | 0.228 | 348    | 351    | +0.9   | 355     | +2.0   | ...    | ...    | 345         | -0.9   |
|          | 0.330 | 326    | 328    | +0.6   | 332     | +1.8   | 321    | -1.5   | 320         | -1.8   |
|          | 0.443 | 302    | 305    | +1.0   | 308     | +2.0   | 295    | -2.3   | 296         | -2.0   |
|          | 0.546 | 277    | 285    | +2.9   | 289     | +4.3   | 276    | -0.4   | ...         | ...    |
|          | 0.673 | 256    | 264    | +3.1   | 267     | +4.3   | ...    | ...    | 257         | +0.4   |
|          | 0.777 | 242    | 248    | +2.5   | 251     | +3.7   | 243    | +0.4   | 244         | +0.8   |
|          | 0.865 | 233    | 236    | +1.3   | 238     | +2.1   | 233    | 0.0    | 233         | 0.0    |

TABLE III. Various calculated and experimental (Srivastava and Saxena) thermal conductivity values at 38°C. The units of  $\lambda$  are cal cm<sup>-1</sup> sec<sup>-1</sup> deg<sup>-1</sup>.

| Gas pair | $X_1$  | Exptl. | Rigor. | % Dev. | Approx. | % Dev. | Empir. | % Dev. | Semi-empir. | % Dev. |
|----------|--------|--------|--------|--------|---------|--------|--------|--------|-------------|--------|
| He-Xe    | 0.0000 | 3753   | 3742   | -0.30  | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.1139 | 2582   | 2665   | +3.2   | 2587    | +0.2   | 2582   | 0.0    | 2571        | -0.4   |
|          | 0.2603 | 1694   | 1797   | +6.1   | 1704    | +0.6   | ...    | ...    | 1686        | -0.5   |
|          | 0.3460 | 1320   | 1443   | +7.5   | 1354    | +2.6   | 1345   | +1.9   | 1338        | +1.4   |
|          | 0.4963 | 898    | 981    | +9.2   | 910     | +1.3   | 902    | +0.4   | ...         | ...    |
|          | 0.6333 | 616    | 675    | +9.6   | 622     | +1.0   | ...    | ...    | 613         | -0.5   |
|          | 0.8991 | 248    | 261    | +5.2   | 241     | -2.8   | 239    | -3.6   | 239         | -3.6   |
|          | 1.0000 | 135    | 144    | +6.7   | ...     | ...    | ...    | ...    | ...         | ...    |
| Ar-Xe    | 0.0000 | 438    | 435    | -0.7   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.1757 | 347    | 338    | -2.6   | 354     | +2.0   | 351    | +1.2   | 346         | -0.3   |
|          | 0.3231 | 292    | 293    | +0.3   | 299     | +2.4   | ...    | ...    | 289         | -1.0   |
|          | 0.5023 | 234    | 240    | +2.6   | 243     | +3.8   | 235    | +0.4   | ...         | ...    |
|          | 0.6727 | 192    | 200    | +4.2   | 199     | +3.6   | 192    | 0.0    | 193         | +0.5   |
|          | 0.7517 | 175    | 184    | +5.1   | 182     | +4.0   | ...    | ...    | 177         | -1.1   |
|          | 0.8339 | 163    | 170    | +4.3   | 165     | +1.2   | 160    | -1.8   | 162         | -0.6   |
|          | 1.0000 | ...    | ...    | ...    | ...     | ...    | ...    | ...    | ...         | ...    |
| Ne-Kr    | 0.0000 | 1180   | 1184   | +0.3   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.0712 | 1035   | 1044   | +1.0   | 1042    | +0.7   | 1028   | -0.7   | 1039        | +0.4   |
|          | 0.2076 | 831    | 831    | 0.0    | 830     | -0.1   | 846    | +1.8   | 825         | -0.7   |
|          | 0.3092 | 696    | 707    | +1.6   | 707     | +1.6   | ...    | ...    | 701         | +0.7   |
|          | 0.4277 | 591    | 588    | -0.8   | 588     | -0.8   | 582    | -1.5   | 583         | -1.3   |
|          | 0.5070 | 516    | 520    | +0.8   | 521     | +1.0   | 515    | -0.2   | ...         | ...    |
|          | 0.6707 | 398    | 403    | +1.3   | 404     | +1.5   | ...    | ...    | 401         | +0.8   |
|          | 0.8556 | 307    | 299    | -2.6   | 290     | -5.5   | 299    | 0.0    | 299         | -2.6   |
|          | 1.0000 | 234    | 232    | -0.9   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 1.0000 | ...    | ...    | ...    | ...     | ...    | ...    | ...    | ...         | ...    |
| Ar-Kr    | 0.0866 | 398    | 404    | +1.5   | 412     | +3.5   | 410    | +3.0   | 412         | +3.5   |
|          | 0.2338 | 366    | 376    | +2.7   | 373     | +1.9   | ...    | ...    | 373         | +1.9   |
|          | 0.3795 | 334    | 343    | +2.7   | 339     | +1.5   | 335    | +0.3   | 339         | +1.5   |
|          | 0.4840 | 317    | 322    | +1.6   | 318     | +0.3   | 314    | -0.9   | ...         | ...    |
|          | 0.6683 | 277    | 287    | +3.6   | 284     | +2.5   | ...    | ...    | 283         | +2.1   |
|          | 0.8115 | 256    | 262    | +2.3   | 261     | +2.0   | 259    | +1.2   | 260         | +1.6   |
|          | 1.0000 | ...    | ...    | ...    | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 1.0000 | ...    | ...    | ...    | ...     | ...    | ...    | ...    | ...         | ...    |
| Ar-He    | 0.1412 | 2693   | 2668   | -0.9   | 2812    | +4.4   | 2737   | +1.7   | 2702        | +0.3   |
|          | 0.2302 | 2247   | 2190   | -2.3   | 2363    | +5.2   | ...    | ...    | 2236        | -0.5   |
|          | 0.4164 | 1538   | 1494   | -2.9   | 1653    | +7.5   | 1524   | -0.9   | ...         | ...    |
|          | 0.6084 | 1037   | 1017   | -1.9   | 1133    | +9.3   | ...    | ...    | 1054        | +1.6   |
|          | 0.8398 | 657    | 632    | -3.8   | 679     | +3.3   | 640    | -2.6   | 648         | -1.4   |
| Ar-Ne    | 0.1183 | 1047   | 1053   | +0.6   | 1031    | -1.5   | 1042   | -0.5   | 1041        | -0.6   |
|          | 0.1370 | 1025   | 1031   | +0.6   | 1010    | -1.5   | ...    | ...    | 1021        | -0.4   |
|          | 0.3124 | 839    | 864    | +3.0   | 839     | 0.0    | 857    | +2.1   | 855         | +1.1   |
|          | 0.3472 | 830    | 835    | +0.6   | 810     | -2.4   | 828    | -0.2   | 826         | -0.5   |
|          | 0.4215 | 768    | 774    | +0.8   | 752     | -2.1   | 770    | +0.3   | ...         | ...    |
|          | 0.6683 | 607    | 609    | +0.3   | 593     | -2.3   | ...    | ...    | 604         | -0.5   |
|          | 0.8286 | 515    | 519    | +0.8   | 511     | -0.8   | 519    | +0.8   | 518         | +0.6   |
|          | 0.8381 | 516    | 514    | -0.4   | 507     | -1.7   | 514    | -0.4   | 513         | -0.6   |
|          | 0.8660 | 503    | 499    | -0.8   | 494     | -1.8   | 500    | -0.6   | 499         | -0.8   |
|          | 1.0000 | ...    | ...    | ...    | ...     | ...    | ...    | ...    | ...         | ...    |

TABLE IV. Various calculated and experimental (von Ubisch) thermal conductivity data at 29°C. The units of  $\lambda$  are cal cm<sup>-1</sup> sec<sup>-1</sup> deg<sup>-1</sup>.

| Gas pair | $X_1$ | Exptl. | Rigor. | % Dev. | Approx. | % Dev. | Empir. | % Dev. | Semi-empir. | % Dev. |
|----------|-------|--------|--------|--------|---------|--------|--------|--------|-------------|--------|
| He-Xe    | 0.000 | 3670   | 3702   | +0.9   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.213 | 1882   | 2011   | +6.9   | 1958    | +4.0   | 1855   | -1.4   | 1910        | +1.5   |
|          | 0.283 | 1530   | 1679   | +9.7   | 1622    | +6.0   | ...    | ...    | 1580        | +3.3   |
|          | 0.582 | 717    | 776    | +8.2   | 741     | +3.3   | 690    | -3.8   | ...         | ...    |
|          | 0.798 | 357    | 394    | +10.3  | 379     | +6.2   | ...    | ...    | 369         | +3.3   |
|          | 1.000 | 143    | 140    | -2.1   | ...     | ...    | ...    | ...    | ...         | ...    |
| Ne-Xe    | 0.000 | 1237   | 1170   | -5.4   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.330 | 596    | 589    | -1.2   | 603     | +1.2   | ...    | ...    | 593         | -0.5   |
|          | 0.430 | 486    | 486    | 0.0    | 494     | +1.6   | 486    | 0.0    | ...         | ...    |
|          | 0.704 | 279    | 283    | +1.4   | 286     | +2.5   | ...    | ...    | 281         | +0.7   |

TABLE IV. (Continued)

| Gas pair | $X_1$ | Exptl. | Rigor. | % Dev. | Approx. | % Dev. | Empir. | % Dev. | Semi-empir. | % Dev. |
|----------|-------|--------|--------|--------|---------|--------|--------|--------|-------------|--------|
| Ar-Xe    | 0.271 | 316    | 308    | -2.5   | 320     | +1.3   | ...    | ...    | 310         | -1.9   |
|          | 0.504 | 239    | 237    | -0.8   | 249     | +4.2   | 240    | +0.4   | ...         | ...    |
|          | 0.750 | 181    | 182    | +0.5   | 190     | +5.0   | ...    | ...    | 184         | +1.6   |
| Kr-Xe    | 0.215 | 206    | 202    | -1.9   | 205     | -0.5   | 216    | +4.9   | 211         | +2.4   |
|          | 0.490 | 186    | 176    | -5.4   | 178     | -4.3   | ...    | ...    | ...         | ...    |
|          | 0.724 | 158    | 158    | 0.0    | 160     | +1.3   | 162    | +2.5   | 166         | +5.1   |
|          | 0.842 | 149    | 150    | +0.7   | 152     | +2.0   | ...    | ...    | 156         | +4.7   |
|          | 0.890 | 145    | 147    | +1.4   | 149     | +2.8   | 145    | 0.0    | 152         | +4.8   |
| He-Kr    | 0.120 | 2610   | 2674   | +2.5   | 2699    | +3.4   | ...    | ...    | 2634        | +0.9   |
|          | 0.250 | 1930   | 1946   | +0.8   | 1980    | +2.6   | 1897   | -1.7   | 1904        | -1.3   |
|          | 0.423 | 1280   | 1302   | +1.7   | 1329    | +3.8   | 1260   | -1.6   | 1265        | -1.2   |
|          | 0.510 | 1030   | 1061   | +3.0   | 1084    | +5.2   | 1026   | -0.4   | ...         | ...    |
|          | 0.578 | 888    | 901    | +1.5   | 920     | +3.6   | 871    | -1.9   | 874         | -1.6   |
|          | 0.760 | 541    | 555    | +2.6   | 567     | +4.8   | ...    | ...    | 542         | +0.2   |
|          | 1.000 | 232    | 226    | -2.6   | ...     | ...    | ...    | ...    | ...         | ...    |
| Ne-Kr    | 0.308 | 716    | 687    | -4.1   | 726     | +1.4   | 724    | +1.1   | 725         | +1.3   |
|          | 0.460 | 568    | 540    | -4.9   | 570     | +0.4   | ...    | ...    | ...         | ...    |
|          | 0.750 | 357    | 343    | -3.9   | 358     | +0.3   | ...    | ...    | 357         | 0.0    |
| Ar-Kr    | 0.298 | 362    | 347    | -4.1   | 355     | -1.9   | ...    | ...    | 358         | -1.1   |
|          | 0.536 | 308    | 298    | -3.2   | 306     | -0.6   | 315    | +2.3   | ...         | ...    |
|          | 0.764 | 272    | 259    | -4.8   | 266     | -2.2   | ...    | ...    | 268         | -1.5   |
| He-Ar    | 0.106 | 2920   | 2897   | -0.8   | 2957    | +1.3   | 2889   | -1.1   | 2899        | -0.7   |
|          | 0.276 | 2020   | 2030   | +0.5   | 2126    | +5.2   | 2031   | +0.5   | 2046        | +1.3   |
|          | 0.541 | 1220   | 1205   | -1.2   | 1279    | +4.8   | ...    | ...    | ...         | ...    |
|          | 0.710 | 843    | 855    | +1.4   | 904     | +7.2   | ...    | ...    | 867         | +2.8   |
|          | 1.000 | 434    | 426    | -1.8   | ...     | ...    | ...    | ...    | ...         | ...    |
| Ne-Ar    | 0.237 | 951    | 917    | -3.6   | 938     | -1.4   | ...    | ...    | 966         | +1.6   |
|          | 0.423 | 798    | 763    | -4.4   | 766     | -4.0   | 792    | -0.8   | ...         | ...    |
|          | 0.642 | 629    | 615    | -2.2   | 613     | -2.5   | 633    | +0.6   | 637         | +1.3   |
|          | 0.842 | 519    | 502    | -3.3   | 505     | -2.7   | ...    | ...    | 516         | -0.6   |
| He-Ne    | 0.119 | 3220   | 3162   | -1.8   | 3271    | +1.6   | 3171   | -1.5   | 3164        | -1.7   |
|          | 0.130 | 3120   | 3117   | -0.1   | 3235    | +3.7   | 3130   | +0.3   | 3122        | +0.1   |
|          | 0.382 | 2340   | 2291   | -2.1   | 2514    | +7.4   | ...    | ...    | ...         | ...    |
|          | 0.755 | 1570   | 1510   | -3.8   | 1676    | +6.8   | ...    | ...    | 1585        | +1.0   |

TABLE V. Various calculated and experimental (von Ubisch) thermal conductivity data at 520°C. The units of  $\lambda$  are cal cm<sup>-1</sup> sec<sup>-1</sup> deg<sup>-1</sup>.

| Gas pair | $X_1$ | Exptl. | Rigor. | % Dev. | Approx. | % Dev. | Empir. | % Dev. | Semi-empir. | % Dev. |
|----------|-------|--------|--------|--------|---------|--------|--------|--------|-------------|--------|
| He-Xe    | 0.000 | 7360   | 7128   | -3.2   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.213 | 3960   | 3982   | +0.6   | 4134    | +4.4   | ...    | ...    | 3875        | -2.1   |
|          | 0.283 | 3270   | 3348   | +2.4   | 3469    | +6.1   | 3276   | +0.2   | 3218        | -1.6   |
|          | 0.582 | 1490   | 1590   | +6.7   | 1635    | +9.3   | ...    | ...    | ...         | ...    |
|          | 0.798 | 770    | 832    | +8.0   | 854     | +10.9  | 804    | ...    | 790         | +2.5   |
|          | 1.000 | 334    | 322    | -3.6   | ...     | ...    | ...    | ...    | ...         | ...    |
| Ne-Xe    | 0.000 | 2360   | 2222   | -5.8   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.330 | 1240   | 1186   | -4.4   | 1255    | +1.2   | ...    | ...    | 1246        | +0.5   |
|          | 0.430 | 1040   | 993    | -4.5   | 1048    | +0.8   | 1034   | -0.6   | ...         | ...    |
|          | 0.704 | 627    | 604    | -3.8   | 632     | +0.8   | ...    | ...    | 628         | +0.2   |
| Ar-Xe    | 0.000 | 914    | 871    | -4.7   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.271 | 681    | 647    | -5.0   | 696     | +2.2   | ...    | ...    | 680         | -0.2   |
|          | 0.504 | 537    | 511    | -4.8   | 554     | +3.2   | 528    | -1.7   | ...         | ...    |
|          | 0.750 | 416    | 404    | -2.9   | 433     | +4.1   | ...    | ...    | 423         | +1.7   |
| Kr-Xe    | 0.000 | 534    | 503    | -5.8   | ...     | ...    | ...    | ...    | ...         | ...    |
|          | 0.215 | 479    | 453    | -5.4   | 474     | -1.0   | ...    | ...    | 479         | 0.0    |
|          | 0.490 | 420    | 400    | -4.8   | 413     | -1.7   | 411    | -2.1   | ...         | ...    |
|          | 0.724 | 358    | 361    | +0.8   | 372     | +3.9   | 361    | +0.8   | 377         | +5.3   |
|          | 0.842 | 341    | 344    | +0.9   | 355     | +4.1   | 343    | +0.6   | 358         | +5.0   |
|          | 0.890 | 338    | 337    | -0.3   | 348     | +3.0   | ...    | ...    | 350         | +3.6   |

TABLE V. (Continued)

| Gas pair | $X_1$ | Exptl. | Rigor. | % Dev. | Approx. | % Dev. | Empir. | % Dev. | Semi-empir. | % Dev. |
|----------|-------|--------|--------|--------|---------|--------|--------|--------|-------------|--------|
| He-Kr    | 0.120 | 5510   | 5216   | -5.3   | 5567    | +1.0   | 5444   | -1.2   | 5455        | +1.0   |
|          | 0.250 | 3900   | 3840   | -1.5   | 4171    | +7.0   | 4028   | +3.3   | 4035        | +3.5   |
|          | 0.423 | 2670   | 2604   | -2.5   | 2858    | +7.0   | 2738   | +2.5   | 2739        | +2.6   |
|          | 0.510 | 2250   | 2138   | -5.0   | 2352    | +4.5   | ...    | ...    | ...         | ...    |
|          | 0.578 | 1950   | 1826   | -6.4   | 2008    | +3.0   | 1922   | -1.4   | 1921        | -1.5   |
|          | 0.760 | 1210   | 1150   | -5.0   | 1260    | +4.1   | ...    | ...    | 1211        | +0.1   |
| Ne-Kr    | 0.308 | 1470   | 1367   | -7.0   | 1490    | +1.4   | ...    | ...    | 1479        | +0.6   |
|          | 0.460 | 1190   | 1097   | -7.8   | 1200    | +0.8   | 1178   | -1.0   | ...         | ...    |
|          | 0.750 | 780    | 727    | -6.8   | 790     | +1.3   | ...    | ...    | 785         | +0.6   |
| Ar-Kr    | 0.298 | 774    | 725    | -6.3   | 768     | -0.8   | ...    | ...    | 761         | -1.7   |
|          | 0.536 | 667    | 634    | -5.0   | 676     | +1.3   | 673    | +0.9   | ...         | ...    |
|          | 0.764 | 596    | 563    | -5.5   | 600     | +0.7   | ...    | ...    | 595         | -0.2   |
| He-Ar    | 0.106 | 5900   | 5616   | -4.8   | 5977    | +1.3   | ...    | ...    | 5941        | +0.7   |
|          | 0.276 | 4220   | 3969   | -5.9   | 4339    | +2.8   | 4234   | +0.3   | 4288        | +1.6   |
|          | 0.541 | 2600   | 2382   | -8.4   | 2639    | +1.5   | ...    | ...    | ...         | ...    |
|          | 0.710 | 1790   | 1704   | -4.8   | 1877    | +4.9   | 1827   | -2.1   | 1852        | +3.5   |
| Ne-Ar    | 0.237 | 1860   | 1767   | -5.0   | 1837    | -1.2   | ...    | ...    | 1880        | +1.1   |
|          | 0.423 | 1580   | 1487   | -5.9   | 1531    | -3.1   | 1539   | -2.6   | ...         | ...    |
|          | 0.642 | 1270   | 1217   | -4.2   | 1251    | -1.5   | 1231   | -3.1   | 1288        | +1.4   |
|          | 0.842 | 1030   | 1012   | -1.7   | 1048    | +1.7   | ...    | ...    | 1066        | +3.5   |
| He-Ne    | 0.110 | 6580   | 6104   | -7.2   | 6514    | -1.0   | 6658   | +1.2   | 6390        | -2.9   |
|          | 0.130 | 6580   | 6019   | -8.5   | 6441    | -2.1   | ...    | ...    | 6309        | -4.1   |
|          | 0.382 | 4740   | 4432   | -6.5   | 4941    | +4.2   | 4927   | +4.0   | ...         | ...    |
|          | 0.755 | 3170   | 2903   | -8.4   | 3238    | +2.1   | ...    | ...    | 3131        | -1.2   |

TABLE VI. Various calculated and experimental data (Srivastava and Saxena) of ternary mixtures at 38°C. The units of  $\lambda$  are cal cm<sup>-1</sup> sec<sup>-1</sup> deg<sup>-1</sup>.

| Gas system | $X_1$  | $X_2$  | $X_3$  | Exptl. | Rigor. | % Dev. | Approx. | % Dev. | Empir. | % Dev. | Semi-empir. | % Dev. |
|------------|--------|--------|--------|--------|--------|--------|---------|--------|--------|--------|-------------|--------|
| He-Ar-Xe   | 0.0733 | 0.6065 | 0.3202 | 843    | 843    | 0.0    | 907     | +7.1   | 836    | -0.8   | 848         | +0.6   |
|            | 0.2424 | 0.3675 | 0.3901 | 845    | 846    | +0.1   | 895     | +5.6   | 836    | -1.1   | 848         | +0.4   |
|            | 0.1319 | 0.1880 | 0.6801 | 1662   | 1654   | -0.5   | 1694    | +1.9   | 1644   | -1.1   | 1656        | -0.4   |
|            | 0.6233 | 0.1800 | 0.1967 | 400    | 402    | +0.5   | 414     | +3.4   | 399    | -0.3   | 404         | +1.0   |
|            | 0.7367 | 0.1495 | 0.1138 | 284    | 285    | +0.4   | 292     | +2.7   | 283    | -0.4   | 285         | +0.4   |
| Ne-Ar-Kr   | 0.2715 | 0.1301 | 0.5984 | 658    | 653    | -0.8   | 651     | -1.1   | 655    | -0.5   | 656         | -0.3   |
|            | 0.3896 | 0.1567 | 0.4537 | 545    | 527    | -3.3   | 531     | -2.6   | 530    | -2.8   | 531         | -2.6   |
|            | 0.3133 | 0.3848 | 0.3019 | 480    | 477    | -0.6   | 470     | -2.1   | 477    | -0.6   | 479         | -0.2   |
|            | 0.1441 | 0.7172 | 0.1387 | 450    | 453    | +0.7   | 451     | +0.2   | 453    | +0.7   | 455         | +1.1   |
|            | 0.6690 | 0.1449 | 0.1861 | 347    | 347    | 0.0    | 347     | 0.0    | 345    | -0.6   | 346         | -0.3   |
|            | 0.7152 | 0.1569 | 0.1279 | 324    | 314    | -3.1   | 317     | -2.2   | 315    | -2.8   | 317         | -2.2   |

mental data on a few systems, also comment on the lack of uniqueness in the values of these empirical constants and determine the range of lower and upper limits. They (1962) also show on the basis of the rigorous Chapman-Enskog first approximation expression for binary viscosity that the corresponding constants are only weakly dependent on temperature and composition. Empirical constants of Table IX do not follow this trend. The reason for this lies primarily in the large flexibility in the values of  $G_{ik}$

and  $G_{ki}$  of Eq. (4). However, these empirical constants still retain their importance for the purpose of representing the composition dependence of  $\lambda_{\text{mix}}$  and in predicting the multicomponent thermal conductivity values. In fact the incentive to the calculation of these two empirical constants ( $G_{ik}$  and  $G_{ki}$ ) was primarily with the idea of evolving the functional dependence of these constants on temperature, molecular weights, and pure thermal conductivity values, etc. If a relation of this type interconnecting

TABLE VII. Various calculated and von Ubisch experimental thermal conductivity data for the He-Kr-Xe system at 29°C. The units of  $\lambda$  are cal cm<sup>-1</sup> sec<sup>-1</sup> deg<sup>-1</sup>.

| $X_1$ | $X_2$ | $X_3$ | Exptl. | Rigor. | % Dev. | Approx. | % Dev. | Empir. | % Dev. | Semi-<br>empir. | % Dev. |
|-------|-------|-------|--------|--------|--------|---------|--------|--------|--------|-----------------|--------|
| 0.695 | 0.086 | 0.219 | 405    | 425    | +4.9   | 412     | +1.7   | 383    | -5.4   | 403             | -0.5   |
| 0.457 | 0.057 | 0.486 | 916    | 939    | +2.5   | 904     | -1.3   | 839    | -8.4   | 878             | -4.1   |
| 0.259 | 0.032 | 0.709 | 1580   | 1658   | +4.9   | 1606    | +1.6   | 1511   | -4.4   | 1565            | -0.9   |
| 0.121 | 0.016 | 0.864 | 2470   | 2488   | +0.7   | 2434    | -1.5   | 2337   | -6.1   | 2394            | -3.1   |
| 0.633 | 0.119 | 0.248 | 455    | 474    | +4.2   | 460     | +1.1   | 428    | -5.9   | 450             | -1.1   |
| 0.438 | 0.082 | 0.480 | 893    | 930    | +4.1   | 898     | +0.6   | 833    | -6.7   | 871             | -2.5   |
| 0.217 | 0.041 | 0.742 | 1710   | 1809   | +5.8   | 1759    | +2.9   | 1662   | -2.8   | 1716            | +0.4   |
| 0.114 | 0.021 | 0.865 | 2390   | 2499   | +4.6   | 2449    | +2.5   | 2357   | -1.4   | 2408            | +0.7   |
| 0.568 | 0.217 | 0.215 | 412    | 434    | +5.3   | 424     | +2.9   | 400    | -2.9   | 416             | +1.0   |
| 0.357 | 0.136 | 0.507 | 964    | 1011   | +4.9   | 983     | +1.9   | 916    | -5.0   | 953             | -1.2   |
| 0.213 | 0.081 | 0.706 | 1520   | 1665   | +9.5   | 1626    | +7.0   | 1532   | +0.8   | 1581            | +4.0   |
| 0.102 | 0.039 | 0.859 | 2380   | 2471   | +3.8   | 2429    | +2.1   | 2337   | -1.8   | 2384            | +0.2   |
| 0.379 | 0.394 | 0.227 | 450    | 475    | +5.6   | 470     | +4.4   | 452    | +0.4   | 461             | +2.4   |
| 0.255 | 0.266 | 0.479 | 928    | 968    | +4.3   | 954     | +2.8   | 898    | -3.2   | 923             | -0.5   |
| 0.133 | 0.138 | 0.729 | 1740   | 1794   | +3.1   | 1772    | +1.8   | 1682   | -3.3   | 1720            | -1.1   |
| 0.071 | 0.073 | 0.856 | 2300   | 2475   | +7.6   | 2451    | +6.6   | 2362   | +2.7   | 2399            | +4.3   |
| 0.162 | 0.593 | 0.245 | 533    | 534    | +0.2   | 538     | +0.9   | 519    | -2.6   | 522             | -2.1   |
| 0.103 | 0.378 | 0.519 | 1060   | 1107   | +4.4   | 1118    | +5.5   | 1053   | -0.7   | 1066            | +0.6   |
| 0.055 | 0.202 | 0.743 | 1840   | 1892   | +2.8   | 1896    | +3.0   | 1811   | -1.6   | 1832            | -0.4   |
| 0.029 | 0.106 | 0.865 | 2500   | 2563   | +2.5   | 2561    | +2.4   | 2480   | -0.8   | 2501            | 0.0    |

TABLE VIII. Various calculated and von Ubisch experimental thermal conductivity data for the He-Kr-Xe system at 520°C. The units of  $\lambda$  are cal cm<sup>-1</sup> sec<sup>-1</sup> deg<sup>-1</sup>.

| $X_1$ | $X_2$ | $X_3$ | Exptl. | Rigor. | % Dev. | Approx. | % Dev. | Empir. | % Dev. | Semi-<br>empir. | % Dev. |
|-------|-------|-------|--------|--------|--------|---------|--------|--------|--------|-----------------|--------|
| 0.695 | 0.086 | 0.219 | 860    | 894    | +3.9   | 927     | +7.8   | 862    | +0.2   | 862             | +0.2   |
| 0.457 | 0.057 | 0.486 | 1990   | 1909   | -4.1   | 1984    | -0.3   | 1843   | -7.4   | 1822            | -8.4   |
| 0.259 | 0.032 | 0.709 | 3450   | 3305   | -4.2   | 3437    | -0.4   | 3241   | -6.1   | 3202            | -7.2   |
| 0.121 | 0.016 | 0.864 | 5080   | 4883   | -3.9   | 5073    | -0.1   | 4884   | -3.9   | 4850            | -4.5   |
| 0.633 | 0.119 | 0.248 | 976    | 991    | +1.5   | 1030    | +5.5   | 956    | -2.0   | 957             | -1.9   |
| 0.438 | 0.082 | 0.480 | 1880   | 1890   | +0.5   | 1969    | +4.7   | 1827   | -2.8   | 1812            | -3.6   |
| 0.217 | 0.041 | 0.742 | 3620   | 3595   | -0.7   | 3745    | +3.5   | 3545   | -2.1   | 3510            | -3.0   |
| 0.114 | 0.021 | 0.865 | 4880   | 4904   | +0.5   | 5101    | +4.5   | 4921   | +0.8   | 4884            | +0.1   |
| 0.568 | 0.217 | 0.215 | 958    | 911    | -4.9   | 952     | -0.6   | 886    | -7.5   | 893             | -6.8   |
| 0.357 | 0.136 | 0.507 | 2030   | 2048   | +0.9   | 2147    | +5.8   | 1997   | -1.1   | 1988            | -2.1   |
| 0.213 | 0.081 | 0.706 | 3390   | 3317   | -2.2   | 3474    | +2.5   | 3330   | -1.8   | 3257            | -3.9   |
| 0.102 | 0.039 | 0.859 | 4830   | 4848   | +0.4   | 5060    | +4.8   | 4880   | +1.0   | 4853            | +0.5   |
| 0.379 | 0.394 | 0.227 | 995    | 993    | -0.2   | 1050    | +5.5   | 990    | -0.5   | 995             | 0.0    |
| 0.255 | 0.266 | 0.479 | 1950   | 1962   | +0.6   | 2085    | +6.9   | 1953   | +0.2   | 1952            | +0.1   |
| 0.133 | 0.138 | 0.729 | 3780   | 3559   | -5.8   | 3765    | -0.4   | 3577   | -5.4   | 3570            | -5.6   |
| 0.071 | 0.073 | 0.856 | 5340   | 4852   | -9.1   | 5100    | -4.5   | 4927   | -7.7   | 4918            | -7.9   |
| 0.162 | 0.593 | 0.245 | 1140   | 1131   | -0.8   | 1197    | +5.0   | 1145   | +0.4   | 1144            | +0.4   |
| 0.103 | 0.378 | 0.519 | 2250   | 2229   | -0.9   | 2411    | +7.2   | 2289   | +1.7   | 2287            | +1.6   |
| 0.055 | 0.202 | 0.743 | 3840   | 3743   | -2.5   | 4009    | +4.4   | 3844   | +0.1   | 3845            | +0.1   |
| 0.029 | 0.106 | 0.865 | 5120   | 5012   | -2.1   | 5306    | +3.6   | 5158   | +0.7   | 5161            | +0.8   |

the two constants could be predicted calculations would be much simpler. Of course semi-empirical procedure involves the assumption of one such relation, Eq. (7), which the empirical constants do not confirm. The implication, however, is not that Eq. (7) is wrong. The inconsistency in the experimental  $\lambda_{\text{mix}}$  values of the three sets of data also may be partially responsible for this anomaly. More confirmatory decision is possible by considering the data on the viscosities of binary mixtures. Saxena

and Singh hope to throw light on this point in a separate publication.

### III. DISCUSSION OF RESULTS

A few recollections are very essential regarding the relative accuracies of the experimental results of these three groups as the data exhibit inconsistencies. Srivastava and Saxena (1957b) used the "thick-wire" variant of the "hot-wire" method which is capable of yielding accurate absolute values of thermal con-



ductivity. These workers claim an uncertainty of 1% in their results. The accuracy of this method is limited by the accuracy and precision attainable in measuring small increments in the resistance of cell wire. A practical way to improve the accuracy, therefore, would be to increase this increment. The possible choices are to use a thin wire either straight or in spiral form. Either choice gives rise to various other uncertainties of doubtful magnitudes which

TABLE IX. Constants  $G_{12}$  and  $G_{21}$  according to various formulas for thermal conductivity.

| Gas pair   | Approximate |          | Empirical |          | Semiempirical |          |
|--|-------------|----------|-----------|----------|---------------|----------|
|  | $G_{12}$    | $G_{21}$ | $G_{12}$  | $G_{21}$ | $G_{12}$      | $G_{21}$ |
| Experimental data of von Ubisch at 29°C            |             |          |           |          |               |          |
| He-Xe  | 0.1410      | 3.596    | 0.258     | 3.913    | 0.146         | 3.765    |
| Ne-Xe  | 0.327       | 2.831    | 0.743     | 2.635    | 0.336         | 2.909    |
| A-Xe   | 0.572       | 1.735    | 1.419     | 1.386    | 0.613         | 1.864    |
| Kr-Xe  | 0.829       | 1.346    | 4.150     | 0.446    | 0.758         | 1.232    |
| He-Kr  | 0.190       | 3.009    | 0.264     | 3.230    | 0.206         | 3.258    |
| Ne-Kr  | 0.434       | 2.317    | 0.423     | 2.350    | 0.437         | 2.328    |
| A-Kr   | 0.756       | 1.415    | 0.811     | 1.241    | 0.742         | 1.388    |
| He-A   | 0.295       | 2.495    | 0.449     | 2.631    | 0.319         | 2.698    |
| Ne-A   | 0.632       | 1.802    | 0.680     | 1.610    | 0.585         | 1.667    |
| He-Ne  | 0.536       | 1.589    | 0.924     | 1.612    | 0.617         | 1.832    |
| Experimental data of von Ubisch at 520°C           |             |          |           |          |               |          |
| He-Xe  | 0.148       | 3.25     | 0.153     | 3.609    | 0.169         | 3.716    |
| Ne-Xe  | 0.352       | 2.489    | 0.414     | 2.496    | 0.357         | 2.521    |
| A-Xe   | 0.598       | 1.637    | 0.189     | 2.660    | 0.633         | 1.732    |
| Kr-Xe  | 0.835       | 1.336    | 2.146     | 0.769    | 0.806         | 1.290    |
| He-Kr  | 0.200       | 2.754    | 0.332     | 2.872    | 0.214         | 2.952    |
| Ne-Kr  | 0.468       | 2.067    | 0.506     | 2.114    | 0.474         | 2.097    |
| A-Kr   | 0.789       | 1.350    | 0.278     | 2.400    | 0.806         | 1.379    |
| He-A   | 0.301       | 2.42     | 0.477     | 2.421    | 0.308         | 2.484    |
| Ne-A   | 0.659       | 1.702    | 1.365     | 1.275    | 0.621         | 1.603    |
| He-Ne  | 0.523       | 1.632    | 0.190     | 2.198    | 0.569         | 1.774    |
| Experimental data of Thornton at 18°C              |             |          |           |          |               |          |
| He-Xe  | 0.134       | 3.727    | 0.200     | 3.800    | 0.134         | 3.598    |
| Ne-Xe  | 0.325       | 2.860    | 1.362     | 2.342    | 0.324         | 2.848    |
| Ar-Xe  | 0.562       | 1.772    | 0.677     | 1.902    | 0.604         | 1.903    |
| Kr-Xe  | 0.819       | 1.365    | 1.158     | 1.068    | 0.801         | 1.334    |
| He-Kr  | 0.189       | 3.054    | 1.363     | 2.609    | 0.193         | 3.124    |
| Ne-Kr  | 0.436       | 2.301    | 1.115     | 1.956    | 0.432         | 2.276    |
| Ar-Kr  | 0.752       | 1.423    | 0.178     | 3.267    | 0.814         | 1.540    |
| Experimental data of Srivastava and Saxena at 38°C |             |          |           |          |               |          |
| He-Xe  | 0.137       | 3.798    | 0.101     | 3.870    | 0.139         | 3.870    |
| Ar-Xe  | 0.555       | 1.802    | 1.116     | 1.553    | 0.593         | 1.924    |
| Ne-Kr  | 0.444       | 2.239    | 0.431     | 2.303    | 0.451         | 2.275    |
| Ar-Kr  | 0.756       | 1.415    | 0.626     | 1.627    | 0.760         | 1.422    |
| He-Ar  | 0.294       | 2.515    | 0.084     | 3.243    | 0.332         | 2.844    |
| Ne-Ar  | 0.647       | 1.744    | 0.597     | 1.690    | 0.621         | 1.674    |

then impair the accuracy of the final results. Thus, von Ubisch (1959) used a thin straight wire and estimates an uncertainty of 4% in his data, while the precision of his measurements was somewhat better,  $\pm 2\%$ . Thornton (1960, 1961) used a spiral form of this wire, the objections against this type of geometry of cell wire have already been pointed out [Srivastava and Saxena (1957b)]. The experimental

error of these measurements is approximately  $\pm 2.2\%$  for low values of  $\lambda_{\text{mix}}$  and this rises to  $\pm 4.0\%$  for high values of  $\lambda_{\text{mix}}$ . However, recent calculations of Saxena and Agrawal (1962) have shown that these  $\lambda_{\text{mix}}$  values possess a great degree of consistency with the binary viscosity data [Thornton (1960, 1961)] which have a better precision of  $\pm 1.0\%$ .

Tables II to V show that the rigorous calculated values of thermal conductivities of binary mixtures are in reasonable agreement with the experimental values with a few exceptions. The most notable case is of the He-Xe system. In all the four sets, the experimental values of  $\lambda_{\text{mix}}$  are always smaller than the computed values by an appreciable amount. The average percentage deviations being +7.3, +6.8, +8.8, and +4.4 for the experimental data of Thornton, Srivastava, and Saxena, von Ubisch at 29°C, and von Ubisch at 520°C, respectively. The maximum percentage deviations in the four cases are +11.6, +9.6, +9.7, and +8.0, respectively. We thus find that the disagreement between theory and experiment for this system is real and cannot be attributed to either any systematic or random errors in the measurements. There are, however, some relative discrepancies among the data of these workers. Mixtures containing up to 50% Xe exhibit good agreement with each other in as much as the three sets of data follow the right type of qualitative trend but for mixtures having higher percentage of Xe there is considerable overlapping and, in fact, for pure Xe, von Ubisch' value is about 6% higher than Saxena's value (1957) in spite of the fact that it corresponds to a temperature which is 9°C lower. Unfortunately only a qualitative comparison is possible, as all the three sets refer to different temperatures. Thornton's (1960, 1961) results are in reasonable agreement with Saxena (1957). The measurements of thermal conductivity [Srivastava and Saxena (1957b), Von Ubisch (1959)] become less accurate for systems which have low  $\lambda$ , and become still worse at low temperatures. He-Xe system is preferable from this viewpoint also and measurements should yield fairly accurate values of  $\lambda_{\text{mix}}$ . Furthermore, the Chapman-Enskog theory holds very well for these monatomic, spherically symmetric molecules. In view of all this it becomes puzzling to account for such an amount of disagreement between theory and experiment which is more than the estimated errors of the measurements. Von Ubisch' measurements at 520°C also exhibit the same trend. The agreement between theory and experiment becomes still worse if we account for the fact that von Ubisch' measurements are about 4%

higher than that of other workers, though for most of the other systems it will improve.

We feel that the fault probably lies with the chosen intermolecular potential for Xe and He-Xe. It will be useful if a check on this point is obtained by interpreting data of some other transport property which is more sensitive to the nature of intermolecular force field. Thermal diffusion data [Atkins *et al.* (1939), Grew (1947), Heymann and Kistemaker (1959)] are available for this system and we propose to investigate it in a later publication. It seems also desirable to redetermine accurately the thermal conductivity of this system as a function of temperature.

For the Ne-Xe system the experimental data of Thornton (1960) and von Ubisch (1959) at 29°C are consistent with each other though the agreement with rigorous theory is poor. The experimental values are consistently greater than the computed values according to rigorous theory. We, thus, find that the Ne-Xe system exhibits departure from the rigorous theoretical values of the opposite sign compared to the He-Xe system. We feel the origin of this discrepancy also lies in sources similar to those for the He-Xe system. For most of the other systems of Thornton the agreement between theory and experiment is satisfactory, the percentage deviation being of the order of experimental uncertainty except in the case of He-Kr and to some extent for Ne-Kr. This inference is also substantiated by the results of von Ubisch given in Table IV. From this latter work we find that the agreement is also poor for Ar-Kr and Ne-Ar systems. On the other hand, the Srivastava and Saxena values (1957b) are in good agreement with the rigorous values for both these systems. Except for the He-Xe system, von Ubisch' experimental values at 520°C (Table V) are systematically larger than the calculated values according to the rigorous theory. Most of the discrepancies found in the case of von Ubisch' data (except the He-Xe system) can be explained if allowance is made for the fact that von Ubisch' experimental data are about 4% higher.

The agreement of the experimental ternary thermal conductivity data with the rigorous theory calculated values is good in the case of mixtures of Table VI. In the case of He-Kr-Xe mixtures at 29°C (Table VII) and 520°C (Table VIII) the agreement is satisfactory and discrepancies which appear are of the same nature as encountered and discussed in the corresponding binary mixtures. As the discrepancies in the related three binary mixtures occur in opposite directions, the integrated effect in ternary

$\lambda_{\text{mix}}$  values is exhibited in somewhat decreased proportions and so the percentage deviation is less in ternary mixtures than some of the related binary mixtures.

The approximate method of calculation seems to be fairly successful in predicting the thermal conductivities of binary and ternary mixtures. Of all the systems investigated by Srivastava and Saxena (1957a, 1957b) and Saxena (1956, 1957), only for the Ar-He system is good agreement not achieved between calculated and experimental values. This also seems to be the case with von Ubisch' data at 29°C, though satisfactory agreement is achieved at 520°C. On the whole, calculated values obtained according to the approximate formula are in reasonable agreement with the experimental data and more elaborate data of good absolute accuracy are required to properly assess this procedure of calculation.

Empirical and semiempirical methods of calculation are about equally successful in predicting the multicomponent thermal conductivity. We feel the reason for this lies in the great success of the form of Eq. (4) for representing  $\lambda_{\text{mix}}$ , so that even an approximate relation connecting  $G_{ik}$  and  $G_{ki}$  [e.g., Eqs. (7) and (8)] serves to reproduce  $\lambda_{\text{mix}}$  values quite precisely. Both of these methods are about equally good, but probably better than the approximate method for calculating multicomponent thermal conductivity of gas mixtures.

#### IV. CONCLUSIONS

The Chapman-Enskog theory of thermal conduction applies well to monatomic, spherically symmetric gases and quite correct values can be obtained if the force law is correctly known. If the force law is not known with confidence, and also the thermal conductivity at one or two compositions, the approximate method is liable to yield the best reliable values. This approach does require the knowledge of pure thermal conductivities at the same temperature which can be generated from the pure viscosity data also. If both viscosity and thermal conductivity data are not available the theoretical formulas in conjunction with the knowledge of force laws for the pure gases may be used. If, however, the thermal conductivity of the binary mixture is also available at one or two compositions the semiempirical and empirical procedures respectively may be used to predict either the entire range or to extend the scope of calculations for predicting the conductivity values for multicomponent mixtures.

This investigation also brings to light the need for accurate determination of thermal conductivities of

pure gases and gaseous mixtures as a function of temperature. The available data are somewhat in disagreement with each other and accurate measurements will clarify the position considerably.

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#### BIBLIOGRAPHY

- Atkins, B. E., Bastick, R. E., and Ibbs, T. L., 1939, Proc. Roy. Soc. (London) **A172**, 142.  
 Chapman, S., 1917, Phil. Trans. **A217**, 115.  
 Chapman, S., and Cowling, T. G., 1952, *The Mathematical Theory of Non-Uniform Gases*, Cambridge University Press, England.  
 Cowling, T. G., 1962, Proc. Roy. Soc. (London) **263A**, 186.  
 Enskog, D., 1911, Physik. Z. **12**, 533.  
 Gray, P., and Wright, P. G., 1961, Proc. Roy. Soc. (London) **263A**, 161.  
 Grew, K. E., 1947, Proc. Roy. Soc. (London) **A189**, 402.  
 Heymann, D., and Kistemaker, J., 1959, Physica **25**, 556.  
 Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., 1954, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, Inc., New York.  
 Lindsay, A. L., and Bromley, L. A., 1950, Ind. Eng. Chem. **42**, 1508.  
 Mason, E. A., 1954, J. Chem. Phys. **22**, 169.  
 ———, 1955, J. Chem. Phys. **23**, 49.  
 ———, 1958, J. Chem. Phys. **28**, 1000.  
 ———, 1960, J. Chem. Phys. **32**, 1832.  
 Mason, E. A., and Saxena, S. C., 1959, J. Chem. Phys. **31**, 511.  
 ———, 1958, Phys. Fluids **1**, 361.  
 Mason, E. A., and von Ubisch, H., 1960, Phys. Fluids **3**, 355.  
 Muckenfuss, C., and Curtiss, C. F., 1958, J. Chem. Phys. **29**, 1273.  
 Saxena, S. C., 1956, J. Chem. Phys. **25**, 360.  
 ———, 1957, Indian J. Phys. **31**, 597.  
 Saxena, S. C., and Agrawal, J. P., 1962, Proc. Phys. Soc. (London) **80**, 313.  
 Saxena, S. C., and Singh, R., 1963, Proc. Phys. Soc. (London) **81**, 788.  
 Srivastava, B. N., and Saxena, S. C., 1957a, J. Chem. Phys. **27**, 583.  
 ———, 1957b, Proc. Phys. Soc. (London) **B70**, 369.  
 Thornton, E., 1960, Proc. Phys. Soc. (London) **76**, 104.  
 ———, 1961, Proc. Phys. Soc. (London) **77**, 1166.  
 von Ubisch, H., 1959, Arkiv Fysik **16**, 93.  
 Wassiljewa, A., 1904, Physik. Z. **5**, 737.  
 Wright, P. G., and Gray, P., 1962, Trans. Faraday Soc. **58**, 1.

### Erratum: The Measuring Process in Quantum Theory

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[Rev. Mod. Phys. **35**, 145 (1963)]

In my paper several lines of explanation in connection with Eq. (22) on p. 148 were omitted. The following lines should be inserted immediately after this equation, and must replace the 4 lines now following it:

"if we make use of  $\sum_m f_{im} f_{im}^* = \delta_{ii}$ , which is necessary as the  $f_{im}$  determine a unitary transformation from a complete set of orthonormal eigenstates  $(\Psi_i)_2$  to another complete set  $\vartheta_m$ .

That the  $(\Psi_i)_2$  indeed form a complete set of

orthonormal eigenstates, as is expressed by Eq. (17), is a consequence of assumption (11). This assumption makes that

$$\Phi_2 = \sum_i a_{ki} (\psi_i)_2 (\Psi_i)_2,$$

which implies that the eigenstates of the complex system formed out of the original system plus the apparatus are determined by products of the form  $(\psi_i)_2 (\Psi_i)_2$ . These can be decomposed into a factor  $(\psi_i)_2$  for the original system, and a second factor  $(\Psi_i)_2$  for the apparatus."

### Erratum: Relativistic Invariance and Hamiltonian Theories of Interacting Particles

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[Rev. Mod. Phys. **35**, 350 (1963)]

In Sec. IV of this paper we have used an "angular momentum Helmholtz theorem" due to J. S. Lomont and H. E. Moses [Communs. Pure Appl. Math. **14**, 69 (1961)]. Our footnote 25, which refers only to the

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second proof of J. B. Keller, should be corrected accordingly. We should also note that our use of this theorem to establish the standard form of classical mechanical angular momentum is similar to the quantum mechanical proof of J. S. Lomont and H. E. Moses [Nuovo Cimento **16**, 96 (1960)]. We regret these omissions.