CERTAIN METHODS FOR CALCULATING THERMAL CONDUCTIVITY OF MULTICOMPONENT MIXTURES INVOLVING POLYATOMIC GASES

G. P. Gupta, S. Mathur and S. C. Saxena

Department of Physics, University of Rajasthan, Jaipur

(*Received* 27 *May* 66 : *Revised* 1 *Dec.* 67)

The assessment of appropriateness of several computing methods for calculating thermal conductivity of mixtures involving polyatomic gases has been investigated by performing calculations on a large number of actual systems where experimental data are available. The procedures are : the linear and reciprocal mixing rules; a combination of these two; a quadratic expression method; three methods of Hirschfelder, Curtiss and Bird; and Lindsay-Bromley method. Nineteen different binary gas-pairs and six ternary systems have been considered. This work will help in predicting thermal conductivity of mixtures in respect of which directly measured values are not available.

Experimental data on thermal conductivity of multicomponent gas mixtures are very useful for a variety of important applied problems involving heat transfer. The data of this type are very scarce particularly when the temperature is increased or the molecules become complicated. Consequently, reliable and simple methods of prediction are of great practical utility. Gandhi & Saxena[1] have recently investigated a series of methods as regards their appropriateness against known λ_{mix} values for monatomic gases.

The phenomenon of thermal conduction in mixtures of polyatomic gases is not very adequately understood as yet. Three different theories[2-4], which have appeared so far, are fairly complicated and differ in their degree of rigour. Without going into their relative merit or appropriateness it is proposed to apply some of the simpler methods, already found dependable in the case of monatomic gases, to predict the thermal conductivity (λ_{mix}) of mixtures involving polyatomic gases and assess the adequacy of each procedure.

METHODS OF COMPUTATION

The various methods of computation are :

(*i*) Linear and reciprocal mixing rules

(*ii*) Combination of these two[5]

(*iii*) Quadratic expression method[6]

(*iv*) Lindsay-Bromley[7] method

and (*v*) Three methods of Hirschfelder *et al*[8]

Gandhi & Saxena[1] have discussed all these methods except (*v*) which are elaborated below.

Hirschfelder *et al*[8] have suggested to compute λ_{mix} for binary systems from the following expressions:

$$\lambda_{mix} = \lambda^{\circ}_{mix} \, (E_1 X_1 + E_2 X_2) \tag{1}$$

where X_i is the mole fraction of the pure ith component and

$$E_i = \frac{\lambda_{i\ exptl}}{\lambda^{\circ}_i} = \frac{\lambda_{i\ exptl}}{\eta_i} \frac{4\ M}{15\ R} \tag{2}$$

where M_i, λ_i & λ°_i are the molecular weight, thermal conductivity, and thermal conductivity with all the internal degrees of freedom frozen of the pure ith component respectively, and λ°_{mix} is the thermal conductivity of the mixture that will be obtained when all the internal degrees of freedom of polyatomic molecules are frozen, η_i is either the experimental or theoretical value of viscosity and R, the gas constant.

We suggest a generalization of equation (1) for a multicomponent mixture in a straight forward manner such that

$$\lambda_{mix} = \lambda^{\circ}_{mix} \sum_{i=1}^{n} X_i\ E_i \tag{3}$$

They have also suggested a second method in which an adjusted value of the collision diameter σ'_i is determined from the experimental value of λ_i and the theoretical knowledge of the potential parameter ϵ_i/k as determined from viscosity. Next the diffusion coefficient is calculated from the values of ϵ_{12}/K and σ'_{12} obtained by using the geometric and arithematic mean rules respectively and the corresponding pure parameters. Thus, knowing the diffusion coefficient, λ_{mix} is calculated from the expression given by Muckenfuss & Curtiss[9]. This method can be readily extended to multicomponent mixtures.

They[8] have further suggested a third method which makes use of the fact that linear proportionality between thermal conductivity and viscosity for pure gases may also hold good for mixtures and suggest that for binary mixtures :

$$\frac{1}{\lambda_{mix}} = \frac{1}{(\eta_{mix})_{exptl}} \left[\frac{X_1^2}{\alpha_1} + \frac{2X_1X_2}{\sqrt{\alpha\alpha_2}} + \frac{X_2^2}{\alpha_2} \right] \tag{4}$$

where $\alpha_i = (\lambda_i / \eta_i)_{exptl}$

NUMERICAL CALCULATIONS

In order to test the real assessment of the various methods discussed in the previous section for computing thermal conductivity of binary and multicomponent mixtures it is essential to perform calculations on such systems where directly observed data are available. We consider here the data collected by the following workers on mixtures mentioned against each :

Cheung *et al*[10] : $He - CH_4$, $He - CO_2$, $O_2 - CO_2$, $CH_4 - C_3H_8$, $CO_2 - C_3H_8$, $N_2 - O_2$ and $N_2 - He$.

Ibbs & Hirst[11] : $N_2 - H_2$, $H_2 - Ar$.

Kornfeld & Hilferding[12] : $H_2 - CO_2$, $H_2 - C_2H_4$.

Keyes[13] & Rothman[14] : $N_2 - CO_2$

Barua[15,16] : $H_2 - Ne$, $H_2 - Xe$, $H_2 - Ne$ and $N_2 - Xe$.

Srivastava & Barua[17] : $O_2 - He$ and $O_2 - Xe$

Weber[18] : $H_2 - CO_2$

Gray & Wright[19] : $N_2 - H_2$
Wassiljewa[20] : $O_2 - H_2$
Devidson & Music[21] : $He - CO_2$, $Ne - CO_2$

These data were plotted to check their smoothness and consistency and found adequate. In fact, we conducted a detailed study[22] of these data to include in our present work only those systems, which did not contain any experimental inconsistency.

Table 1 gives the experimental values in column 4 and the mole-fraction of the heavier component in each case in column 3. The temperature to which the experimental measurements refer are indicated in column 2. The percentage deviations of the calculated values from the experimental λ_{mix} values for the linear, reciprocal, a combination of these two, and quadratic formula, are recorded in columns 5 to 8. The empirical method of Hirschfelder *et al*[8], as elaborated by equation (1) was also tried for all the systems given in Table 1 and the values of percentage deviation so obtained are mentioned in column 9. The second method suggested by Hirshfelder *et al*[8] was also applied to a large number of these systems and the percentage deviation values are given in column 10. Lindsay & Bromley[7] method has been applied by Cheung *et al*[10] to a large number of systems; their percentage deviations are quoted in column 11.

The pure thermal conductivity data required in the calculations of Table 1 were always taken in each case of the same worker as the mixture data.

TABLE 1

COMPARISON OF EXPERIMENTAL AND VARIOUS CALCULATED $\lambda_{mix} \times 10^5$ (CAL CM^{-1} DEG^{-1} SEC^{-1}) VALUES

(*Entries in columns 5 to 11 are percentage deviations*)

Gas Pair	Temp. (°C)	X_1	$\lambda_{Exptl.}$	λ_{SM}	λ_{RM}	λ_C	λ_Q	$\lambda_{HCB(1)}$	$\lambda_{HCB(2)}$	λ_{LB}
1	2	3	4	5	6	7	8	9	10	11
$He—CH_4$	316	0·254	40·63	+14·8	—5·1	+4·8	—2·5	+8·7	+2·5	—0·5
		0·45	30·54	+30·0	+2·1	+16·1	—	+21·3	+10·7	+7·6
		0·701	24·53	+25·8	+2·1	+13·9	—5·9	+18·3	+7·6	+6·0
$He—CO_2$	0	0·26	17·83	+42·8	—43·4	—0·3	+9·5	+2·1	+3·5	—3·1
		0·48	11·20	+68·2	—43·2	+11·9	—	+5·8	+4·6	—6·3
		0·75	6·35	+70·9	—31·2	+19·8	—20·3	+7·1	+3·3	—5·4
	316	0·39	23·65	+59·2	—18·2	+20·5	—	+25·4	+18·5	+10·3
$H_2—CO_2$	0	0·1686	27·99	+25·7	—48·7	—11·5	+6·1	+2·8	—	—2·5
		0·3932	17·24	+54·3	—55·5	—0·6	—	+5·7	—	—3·2
		0·6302	10·34	+69·5	—50·3	+9·6	—18·8	+6·1	—	—4·9
		0·8299	6·073	+63·0	—33·8	+14·6	—28·2	+6·9	—	—2·6
	25	0.0362	40·2	+5·2	—19·6	—7·2	+2·2	—0·5	—0·2	—0·2
		0·0941	35·0	+14·3	—34·9	—10·3	+5·7	—0·3	+0·3	+0·3
		0·504	15·13	+56·8	—51·0	+2·9	—	—2·0	—2·7	—2·6
		0·807	7·58	+54·7	—34·9	+10·0	—16·0	—1·7	—3·4	—3·4
		0·953	4·43	+34·1	— 3·8	+15·1	—0·7	+9·0	+8·1	+8·4
$H_2—C_2H_4$	25	0·1351	32·9	+17·0	—33·1	—7·9	+5·5	—1·5	—0·6	—1·5
		0·389	20·6	+39·8	—44·7	—2·5	+1·9	—2·9	—0·4	—5·3
		0·4863	16·90	+48·0	—43·1	+2·4	—	—1·0	—2·7	—4·6
		0·686	11·48	+51·0	—36·6	+7·2	—9·9	—0·6	—3·7	—5·4
		0·8302	8·61	+37·2	—28·0	+0·5	—16·1	—3·0	—6·0	—7·2
$O_2—N_2$	319	0·6098	11·19	+0·6	+0·4	+0·5	—	+0·3	+0·2	+0·5

TABLE I—(*contd.*)

Gas Pair	Temp. (°C)	X_1	$\lambda_{Exptl.}$	λ_{SM}	λ_{RM}	λ_C	λ_Q	$\lambda_{HCB(1)}$	$\lambda_{HCB(2)}$	λ_{LB}
1	2	3	4	5	6	7	8	9	10	11
O_2—CO_2	97	0·222	7·027	+1·3	—1·3	+0·0	—0·3	+7·4	+0·0	—0·9
		0·464	6·383	+2·3	—1·4	+0·4	—	+3·9	+0·3	—0·7
		0·685	5·883	+1·8	—1·4	+0·2	—0·6	+1·4	+0·0	—1·6
		0·73	5·777	+1·7	—1·2	+0·3	—0·5	+1·2	+0·1	—0·7
N_2—CO_2	50	0·335	5·67	+3·4	—0·5	+1·6	+0·5	+1·9	+1·6	+1·6
		0·4712	5·37	+3·5	—1·1	+1·3	—	+1·7	+1·3	+0·9
		0·6594	4·99	+2·6	—1·4	+0·6	—0·6	+1·0	+0·6	+0·6
	250	0.335	9·36	—0·2	—0·9	—0·5	+0·4	+1·1	—1·2	—0·2
		0·4712	9·21	—0·8	—1·4	—1·1	—	+0·7	—1·8	—1·2
		0·6594	8·91	—0·6	—1·1	—0·8	+0·2	+0·7	—1·6	—0·3
	573	0·33	14·19	—4·5	—4·6	—4·5	—1·1	—1·5	—6·1	—3·4
		0·50	14·17	—3·8	—3·8	—3·8	—	—0·6	—5·7	—3·0
		0·67	14·03	—2·3	—2·3	—2·3	+1·1	+0·5	—3·1	—1·6
	688	0·25	16·29	—4·5	—4·5	—4·5	—1·1	—1·7	—5·9	—3·7
		0·50	16·51	—4·4	—4·5	—4·5	—	—1·0	—6·4	—3·5
		0·75	16·44	—2·6	—2·8	—2·6	+0·6	—0·4	—4·3	—2·2
C_3H_8—CH_4	95	0·221	8·841	+8·3	+3·7	+6·0	+2·7	+9·1	+3·4	+7·9
		0·514	7·636	+9·5	+2·8	+6·2	—	+10·4	+0·3	+2·3
		0·687	7·083	+7·9	+2·2	+5·1	—0·9	+8·5	+0·7	+1·4
C_3H_8—CO_2	95	0·365	5·715	—1·9	—2·8	—2·4	—0·9	+9·8	—4·6	0·0
		0·551	5·884	—1·1	—2·1	—1·6	—	+10·6	—2·9	+0·7
		0·709	6·083	—1·3	—2·1	—1·7	—0·4	+7·7	—2·4	0·0
N_2—H_2	0	0·841	8·0	+37·5	—20·3	+8·6	—7·5	+1·3	—	+2·3
		0·610	12·7	+50·4	—53·2	+7·9	—	+2·4	—	+3·9
		0·348	19·4	+45·9	—54·0	+5·7	+13·9	+8·8	—	+10·3
		0·197	25·7	+32·3	—30·0	+1·2	+14·0	+7·8	—	+8·9
	149·3	0·082	47·25	+6·3	—21·8	—7·7	+1·3	—	—	—
		0·1415	41·8	+13·6	—28·2	—7·2	+4·5	—	—	—
		0·3105	32·1	+24·0	—38·9	—7·5	+2·8	—	—	—
		0·504	23·0	+34·3	—38·7	—2·2	—	—	—	—
		0·6045	19·1	+37·7	—35·6	+1·0	—2·1	—	—	—
		0·711	15·7	+36·3	—31·7	—2·5	—5·1	—	—	—
		0·814	12·7	+31·5	—23·9	—3·9	—6·3	—	—	—
		0·853	12·1	+23·1	—23·1	0·0	—9·9	—	—	—
H_2—Ne	30	0·85	14·25	+14·9	—8·2	+3·4	+0·4	—2·9	—	—
		0·70	17·74	+18·9	—15·9	—1·5	—0·3	—6·1	—	—
		0·55	21·80	+18·5	—20·4	—1·0	—	—7·1	—	—
		0·40	26·58	+15·0	—22·0	—3·5	+0·3	—6·1	—	—
		0·25	32·24	+9·4	—20·1	—5·3	0·0	—5·6	—	—
		0·10	38·88	+2·9	—12·6	—4·9	—0·8	—3·6	—	—
H_2—Xe	30	0·85	3·745	+101·5	—60·6	+20·5	+75·7	—14·1	—	—
		0·70	6·812	+103·0	—73·9	+14·6	+79·7	—14·2	—	—
		0·55	10·61	+89·6	—78·9	+5·4	—	—11·0	—	—
		0·40	15·81	+67·0	—80·9	—7·0	+55·5	—8·6	—	—
		0·25	21·68	+50·8	—78·6	—13·9	+44·2	0·0	—	—
		0·10	33·49	+16·4	—70·2	—26·9	+14·3	—2·7	—	—
N_2—R	30	0·15	26·60	+19·6	—21·6	—1·0	+5·3	+2·1	—	—
		0·30	19·83	+37·6	—26·3	+5·6	+5·9	+2·9	—	—
		0·45	15·34	+48·2	—35·5	+10·8	—	+6·7	—	—
		0·60	11·52	+58·0	—20·6	+18·7	—4·3	+11·2	—	—
		0·75	9·310	+46·7	—17·2	+14·7	—13·4	+6·7	—	—
		0·90	7·401	+23·3	—10·1	+6·6	—13·0	+1·6	—	—
	316	0·695	16·21	+50·2	—12·9	+18·7	—12·2	—	—	+8·2
		0·363	28·24	+39·1	—22·3	+8·4	—	—	—	+4·8
		0·261	33·47	+31·1	—21·0	+5·0	+3·6	—	—	+4·5

TABLE 1 (*contd.*)

Gas Pair	Temp. (°C)	X_1	$\lambda_{Exptl.}$	λ_{SM}	λ_{RM}	λ_C	λ_Q	$\lambda_{HCB(1)}$	$\lambda_{HCB(2)}$	λ_{LB}
1	2	3	4	5	6	7	8	9	10	11
O_2—He	30	0·15	27·00	+18·1	−20·6	−1·3	+21·3	+1·9	—	—
		0·30	20 14	+36·0	−24·6	+5·7	+43·2	+6·1	—	—
		0·45	15·64	+46·4	−24·7	+10·9	—	+7·0	—	—
		0 60	12·30	+49·7	−21·9	+13·9	+63·2	+7·7	—	—
		0·75	9·642	+44·4	−15·9	+14·2	+57·9	+7·1	—	—
		0·90	7·621	+23·8	−7·9	+8·0	+38·0	+3·4	—	—
Ne—CO_2	0	0·74	4·47	+19·0	−7·6	+5·8	+1·8	+12·8	—	+3·3
		0·53	5·88	+17·0	−14·8	+1·2	—	+10 2	—	−0·2
		0·40	6 79	+15·6	−15·0	+0·3	+1·3	+9·6	—	−1·5
		0·31	7·31	+16·6	−11·9	+2·3	+4·8	+11·4	—	+2·8
O_2—Xe	30	0·85	1·684	+22·7	−12·7	+5·0	−2·0	−2·6	—	—
		0·70	2·223	+27·7	−23·4	+2·1	−3·1	−6·6	—	—
		0·55	2·804	+28·8	−27·9	+0·4	—	−6·8	—	—
		0·40	3·564	+23·0	−30·2	−3·6	+1·0	−6·7	—	—
		0·25	4·301	+19·9	−24·9	−2·5	+5·6	−1·7	—	—
		0·10	5·500	+7·8	−16·2	−4·2	+2·4	−1·4	—	—
N_2—Xe	30	0·85	1·698	+16·7	−16·1	+0·3	+10·4	−5·3	—	—
		0·70	2·139	+26·6	−23·0	+1·8	+18·4	−4·5	—	—
		0·55	2·630	+30·6	−25·8	+2·4	—	−1·7	—	—
		0·40	3·297	+26·2	−27·3	−0·5	+20·2	−1·2	—	—
		0·25	4·135	+18·2	−25·0	−3·4	+14·4	−0·6	—	—
		0·10	5·175	+8·5	−15·0	−3·2	+7·1	+0·4	—	—
H_2—Ar	0	0·82	7·3	+43·8	−36·2	+4·1	−6·8	−11·0	—	−2·1
		0·60	12·6	+46·8	−51·5	−2·4	—	−11·9	—	−3·1
		0·40	18·7	+38·0	−54·4	−8·0	+6·4	−8·6	—	−1·0
		0·198	27·0	+23·0	−47·6	−12·2	+8·5	−0·3	—	−1·4
H_2—O_2	22	0·50	18·27	+31·5	−40·5	−4·5	—	−5·6	—	—

NOTE 1—λ_{SM}, λ_{RM}, λ_C, λ_Q, $\lambda_{HCB(1)}$, $\lambda_{HCB(2)}$ and λ_{LB} are the values of mixture conductivity calculated according to simple mixing rule, reciprocal mixing rule, a combination of simple and reciprocal mixing rules, quadratic expression, Hirschfelder, Curtis & Bird Method (1), Method (2) and Lindsay—Bromley method respectively.

NOTE 2—Dash (—) stands for uncalculated thermal conductivity values.

Experimental data for the following six different ternary systems involving polyatomic gases were available :

Cheung *et al*[10] : $N_2 — O_2 — CO_2$, $He — N_2 — Ar$, $He — CH_4 — N_2$
Clingman *et al*[23] : $He — CH_4 — O_2$, $Ar — CH_4 — O_2$
Gruss & Schmick[24] : $N_2 — CH_4 — O_2$

All these data are reported in Table 2. The percentage deviations of the calculated values from the experimental λ_{mix} values for the linear, reciprocal and a combination of these two, are also recorded in Table 2. We have not extended the other methods in view of their complexity, but the calculations were performed for the $N_2 — O_2 — CO_2$ system for the three other methods. Hirschfelder *et al*[8] method given by equation (3) reproduces the experimental data within 0·8%. The second method by these very authors also turns out to be equally satisfactory and reproduces the experimental values within 0·5%. Lindsay & Bromley[7] method succeeds in reproducing the experimental

TABLE 2

EXPERIMENTAL AND CALCULATED $\lambda_{mix} \times 10^5$ (CAL CM^{-1} SEC^{-1} DEG^{-1}) VALUES FOR SEVERAL TERNARY MIXTURES (*Columns 7, 8 and 9 give absolute percentage deviations*)

Gas System	Temp. (°C)	X_1	X_2	X_3	$\lambda_{Exptl.}$	λ_{SM}	λ_{RM}	λ_C
1	2	3	4	5	6	7	8	9
N_2—O_2—CO_2	97·0	0·3231	0·3729	0·3040	6·729	+1·2	−1·6	−0·1
Ar—N_2—He	99·5	0·117	0·468	0·415	13·95	+53·6	−27·1	+14·0
N_2—CH_4—He	317·0	0·476	0·365	0·159	16·74	+27·5	−8·7	+9·4
O_2—CH_4—He	0·0	0·197	0·060	0·743	20·0	+34·5	−22·0	+6·5
		0·188	0·100	0·712	19·5	+33·8	−23·6	+5·1
		0·181	0·135	0·684	18·6	+36·0	−23·1	+6·5
Ar—O_2—CH_4	0·0	0·751	0·199	0·050	4·59	−2·4	−5·9	−4·1
		0·712	0·188	0·100	4·71	−1·9	−6·4	−4·0
		0·677	0·179	0·144	4·91	−3·3	−8·6	−5·9
O_2—N_2—CH_4	0·0	0·194	0·736	0·070	5·90	−1·4	−1·7	−1·5
		0·188	0·712	0·100	5·99	−2·0	−2·5	−2·2
		0·185	0·698	0·117	6·01	−2·0	−2·5	−2·2
	22·0	0·185	0·739	0·076	6·13	+2·0	+1·8	+2·0
		0·122	0·488	0·390	6·50	+1·2	+0·6	+0·9
		0·060	0·240	0·700	6·87	+0·6	0·0	+0·3
		0·024	0·096	0·880	7·08	+0·0	0·0	0·0
Average deviation (%)						17·5	10·0	5·3

values within 0·9%. Cheung, *et al*[10] have also reported the computed values of λ_{mix} according to the Lindsay—Bromley formula for the systems $He - CH_4 - O_2$, $Ar - CH_4 - O_2$, $He - N_2 - Ar$ and $He - CH_4 - N_2$. The average absolute deviations for these systems are 3·9, 3·9, 5·0 and 6·1% respectively.

DISCUSSION

A close examination of Tables 1 and 2 shows that the linear mixing rule, in general, overestimates the values of λ_{mix} by an appreciable amount. In general the discrepancy is more pronounced when the two components have widely different thermal conductivity values. Similarly the reciprocal mixing rule underestimates the λ_{mix} values and it also turns out to be a relatively poor method for mixtures whose constituents differ a lot in conductivity. These opposite trends in the variation of the calculated values from the experimental values and further the way these discrepancies increase for a particular mixture suggest that a combination of two might successfully be employed for a very simple choice of predicting λ_{mix}. It is found that this method is on the whole reasonably satisfactory for purposes of approximate prediction of λ_{mix}. It also impresses by its simplicity.

The quadratic method has on the other hand two distinct disadvantages: (*i*) it requires one λ_{mix} value and (*ii*) the computations according to this method are somewhat tedious from the computational view point. For the same reason this method leads to values which are in good agreement with the experimental values. The overall success of this procedure is somewhat better than that of the simple mixing rules mentioned above. The semi-theoretical procedure (suggested by present authors[25,26]) which also requires one λ_{mix} value, works better than this procedure. These circumstances make this method of rather doubtful validity and promise.

The method of equations (1) and (2) was put to test by Hirschfelder *et al*[8], the introducers of this method, for seven different binary gas-pairs and 36 mixtures. The average absolute deviation is maximum for $H_2 - Ar$ (9·4%) and minimum for $H_2 - CO_2$ (1·6%); for all the systems its value is 5·4%. In this paper 19 different gas-pairs were tried and it was found that the general agreement between theory and experiment is of the same type as found earlier[8]. The average absolute deviation for all the systems is 6·0%. The only advantage of this method seems to lie in the fact that only important information needed is the conductivity of the related pure components. However, it may be pointed out that adequate knowledge of the force laws is also needed and this may not be available always specially when complicated and uncommon gases are involved. It is fairly laborious and unhandy for actual calculations. In view of the overall success of this method and the facts mentioned above it does not seem to inspire any special preference. The idea behind performing such laborious calculations for such a large number of systems was to reliably discover the statistical expectation of its accuracy. These calculations could not confirm the optimism by reducing the average expected uncertainty.

The second method suggested by Hirschfelder *et al*[8] is fairly tedious in as much as it requires extraordinary amount of labour. These authors[8] did not themselves apply this method of computation to actual systems although it has adjustments because of which it is likely to lead to good agreement between theory and experiments. We have therefore adopted this method and applied it to 9 different gas-pairs and 40 mixtures. In general, this method is quite dependable and invariably leads to values which are in agreement with the experimental values within the limits of experimental uncertainties (see Table 1). The average absolute deviation for all the mixtures is 4·1%. The discrepancy in the case of $He—CO_2$ at 316°C is very large (18·5%). In case we take notice of the fact that in other methods also the discrepancies observed for this single mixture are large, we can ignore it and then the average absolute deviation improves to 2·9%. Another very important observation of value in connection with the assessment of this method is obtained from a critical examination of Table 1. For all the systems at high temperatures this method seems to become somewhat inferior and the agreement between theory and experiment becomes worst. This is unfortunately a somewhat disappointing feature of this method and may be further confirmed when reliable data become available. The basis for the suggestion of this future work lies in the remarkable reproduction of λ_{mix} value for $O_2 - N_2$ at 319°C. Thus we find that though this method involves laborious computation it has good potentiality.

The third method of Hirschfelder *et al*[8], as given by equation (4), is physically unsound and requires experimental values of the viscosity and the thermal conductivity of pure components in addition to mixture viscosity. Well knowing these disadvantages Hirschfelder *et al*[8] put this method to test for seven systems. Their calculated values are in poor agreement with the experimental values. The average absolute deviation is minimum for $H_2 - N_2$ system (9·4%) and is maximum for $N_2 - Ar$ (55·9%). The average number for all the seven systems is 22·7%.

It will be appropriate to discuss now the Lindsay-Bromley formula so often employed with moderate success. Such calculations have already been reported by Cheung *et al*[10]. Their data for 14 systems are reproduced in Table 1. It will be noted that the predicted values roughly agree with the experimental values and the average absolute deviation for all the systems is 3·4%. This confirms once again the earlier observation of Srivastava & Saxena[27] and Saxena[28] at Lindsay-Bromley formula needs to be improved for precise reproduction.

For obtaining more precise quantitative assessment of different computational procedures for a gas-pair, the average absolute deviations (of computed values from experimental values) systemwise are given in Table 3. It also gives mean values for all the systems. We hope this will help either (*i*) in choosing a method once the gas-pair and other conditions are fixed or (*ii*) in assessing the accuracy of a particular value on a specific method.

TABLE 3

AVERAGE ABSOLUTE PERCENTAGE DEVIATION SYSTEMWISE OF COMPUTED VALUES FROM EXPERIMENTAL VALUES

Gas-pair	Temp. (°C)	λ_{SM}	λ_{RM}	λ_{C}	λ_{Q}	$\lambda_{HCB(1)}$	$\lambda_{HCB(2)}$	λ_{LB}
$He—CH_4$	316	23·5	3·1	11·6	4·2	16·1	6·9	4·7
$He—CO_2$	0	60·6	39·3	10·7	14·9	5·0	3·8	4·9
	316	59·2	18·2	20·5	—	25·4	18·5	10·3
$H_2—CO_2$	25	33·0	28·8	9·1	6·2	2·7	2·9	3·0
$H_2—C_2H_4$	25	38·6	37·1	4·1	8·4	1·8	2·7	4·8
$O_2—N_2$	319	0·6	0·4	0·5	—	0·3	0·2	0·5
$O_2—CO_2$	97	1·8	1·3	0·2	0·5	3·5	0·1	1·0
$N_2—CO_2$	50	3·2	1·0	1·2	0·6	1·5	1·2	1·0
	250	0·5	1·1	0·8	0·3	0·8	1·5	0·6
	573	3·5	3·6	3·5	1·1	0·9	5·0	2·7
	688	3·8	3·9	3·9	0·9	1·0	5·5	3·1
$C_3H_8—CH_4$	95	8·6	2·9	5·8	1·8	9·3	1·5	3·9
$C_3H_8—CO_2$	95	1·4	2·3	1·9	0·7	9·4	3·3	0·7
$N_2—H_2$	0	41·5	39·4	5·9	11 8	5·1	—	6·3
	149·3	25·9	30·2	4·0	4·6	—	—	—
$H_2—Ne$	30	13·3	16·5	3·3	8·4	5·2	—	—
$H_2—Xe$	30	71·4	73·1	14·4	53·9	8·4	—	—
$N_2—He$	30	38·9	21·9	9·6	8·4	5·2	—	—
	316	40·1	18·7	10·7	7·9	—	—	5·8
$O_2—He$	30	36·4	19·3	9·0	43·5	5·5	—	—
$Ne—CO_2$	0	17·5	12·3	2·4	2·6	11·0	—	1·9
$O_2—Xe$	30	21·7	22·7	3·0	2·8	4·3	—	—
$H_2—Xe$	30	21·1	22·0	1·9	14·1	2·3	—	—
$H_2—Ar$	0	37·9	47·4	6·7	7·2	8·6	—	1·9
$H_2—CO_2$	0	53·1	47·1	9·1	17·7	5·4	—	3·3
$H_2—O_2$	22	31·5	40·5	4·5	—	5·6	—	—
Average deviation (%)		26·5	21·3	6·1	9·3	6·0	4·1	3·4

CONCLUSION

Based on the experience of all these calculation procedures for a large number of gas-pairs over varied conditions of temperature and composition, the following comments and suggestions are offered for help in predicting thermal conductivity under condition where direct measured values may not be available and one may be interested in the knowledge of best estimated value:

1. The linear and reciprocal mixing rules seldom lead to values of reasonable accuracy. The method based on the combination of these two also lacks in precision but offers itself as a crude simple choice.
2. The quadratic equation method is of little interest. Semi-theoretical method requiring an almost identical amount of initial information should be preferred as it is quite dependable.
3. The first method of Hirschfelder *et al*[8] inspires little interest in view of its complexity and lack of precision.
4. The second method of Hirschfelder *et al*[8] is quite a good one provided one can put up with the computational strain.
5. The third method of Hirschfelder *et al*[8] is not accurate and does not impress by the amount of initial information it requires.
6. The original Lindsay-Bromley[7] method seems to entail uncertainty amounting to a couple of percent. The older effort to improve upon it has lost its glamour in view of what is mentioned in 2 above.
7. Though the detailed calculations of this paper are confined to binary systems yet the sample calculations performed for the ternary systems suggest that all the recommendations mentioned above apply to multicomponent systems also.

ACKNOWLEDGEMENT

We are thankful to the Ministry of Defence for supporting this work and awarding research fellowship to one of us, namely G.P. Gupta.

REFERENCES

1. GANDHI, J.M. & SAXENA, S.C., *Indian J. Pure Appl. Phys.*, **4** (1966), 461.
2. HIRSCHFELDER, J.O., "Sixth Internat. Combustion Symp." (Reinhold Publishing Corporation, New York) 1957, p. 351.
3. SAXENA, S.C., SAKSENA, M.P., GAMBHIR, R.S. & GANDHI, J.M., *Physica*, **31** (1965), 333.
4. MONCHICK, L., PEREIRA, A.N.G. & MASON, E.A., *J. Chem. Phys.*, **42** (1965), 3241.
5. BURGOYNE, J.H. & WEINBERG, F., "Fourth Symp. on Combustion", (Williams and Wilkins Co., Baltimore) 1953, pp. 294-302.
6. KENNARD, E H., "Kinetic Theory of Gases", (Mc Graw-Hill Book Co., Inc., New York) 1938, p. 183.
7. LINDSAY, A.L. & BROMLEY, L. A., *Ind. Engg. Chem.*, **42** (1950), 1508.
8. HIRSCHFELDER, J.O., CURTISS, C.F. & BIRD, R.B., "Molecular Theory of Gases and Liquids" (John Wiley and Sons, Inc., New York) 1954, pp 536-537.
9. MUCKENFUSS, C. & CURTISS, C.F., *J. Chem. Phys.*, **29** (1958), 1273.
10. CHEUNG, H., BROMLEY, L.A. & WILKE, C.R., Report No. U.C.R.L. (University of California, Lawerence Radiass Laboratory, Berkley, California) 8230 Rev. (U.S. Atomic Energy Commission), 1959.
11. IBBS, T.L. & HIRST, A.A., *Proc. Royal. Soc.* London **A 123** (1929), 134.
12. KORNFELD, G. & HILFERDING, K., *Z. fur Physik, Chem.* Bodenstein-Festband, (1931), 792.

13. Keyes, F.G., *Trans. Amer. Soc. Mech. Engrs.*, **74** (1952), 1303.

14. Rothman, A.J., "Thermal Conductivity of Gases at High Temperatures"—a Thesis, (University of California), 1954.

15. Barua, A.K., *Physica*, **25** (1959), 1275.

16. Barua, A.K., *Indian J. Phys.*, **34** (1960), 169.

17. Srivastava, B.N. & Barua, A.K., *J. Chem. Phys.*, **32** (1960), 427.

18. Weber, S.T.H., *Ann. Physik.*, **54** (1917), 481.

19. Gray, P. & Wright P.G., *Proc. Royal. Soc.*, London **A23** (1961), 161.

20. Wassiljewa, A., *Physik*, **75** (1904), 737.

21. Davidson, J.M. & Music, J.F., U.S. Atomic Energy Commission Rept. No. H.W. 29021 (1953), p. 7.

22. Saxena, S.C., Mathur, S. & Gupta, G.P., *Def. Sci. J.*, **16A** (1966), 99.

23. Clingman, W.H., Brokaw, R S. & Pease, R.N., "Fourth Internat. Combustion symp. (Williams and Wilkins Company, Baltimore) 1953, p 310.

24. Gruss, H. & Schmick, H., *Wiss*, Veroffentlich Siemens Konzern, **7** (1928), 202.

25. Mathur, S. & Saxena, S.C., *Appl. Sci. Res.*, **17** (1967), 155.

26. Gupta, G.P. & Saxena, S.C., *Def. Sci. J.*, **16** (1966), 165.

27. Srivastava, B.N. & Saxena, S.C., *Proc. Phys. Soc.* (London), **70** (1957), 369.

28. Saxena, S.C., *Indian J. Phys.*, **31** (1957), 597.