PREDICTION OF THERMAL CONDUCTIVITY OF PURE GASES AND MIXTURES

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Inter relations between the various transport properties of gases have been presented which enable to compute and predict the thermal conductivity of pure monoatomic as well as polyatomic gases. Similar relations are also presented for multicomponent mixtures of monoatomic and polyatomic gases. Many calculations have been performed to have a critical assessment of such approaches and for which this work reveals a very good promise. This has encouraged us to predict thermal conductivity of pure gases and mixtures under conditions where the experiments have not been performed but the data are needed in a variety of important applied problems.

Thermal conductivity data of polyatomic gases and gas mixtures besides being important for the understanding of the nature of such molecules, are also useful in a large number of important applied problems. The actual measurement of thermal conductivity specially, at high temperatures, is difficult and also theoretical formulation of this property is not free from ambiguities. Consequently neither sufficient experimental data are available nor reliable theoretical computations are possible. Therefore an attempt has been made to estimate such values by a procedure which is not completely dependent on the theoretical expressions, instead of, it employs expressions in which mostly measurable quantities occur. The basic advantage is that some of the theoretical short comings of this process get somewhat reduced or completely eliminated when experimentally measured quantities are substituted for their theoretical analogs. One of the most important and inherent defect of this approach consists in the obvious fact that one needs a large amount of experimental information. This may not, however, be always a practical handicap for the involved experimental quantities and also may be simpler to measure with better accuracy as compared to thermal conductivity. This situation has provided incentive for the work described in this article.

It may be pointed out that this approach of evaluating one property from its theoretical expression in which almost all quantities have been replaced in favour of one measured property or the other is by no means altogether new. Many transport properties like thermal diffusion, diffusion, viscosity and thermal conductivity of monoatomic gases have been generated on this principle. Most of the earlier work is described in the article by Gandhi and Saxena[1], and since then similar efforts have been made by Weissman[2,3] in predicting mutual diffusion coefficients from thermal conductivity data etc. Mathur & Saxena[4] have also developed a correlation between thermal conductivity of polyatomic gases and gas mixtures and other properties and investigated their appropriateness by performing calculations for those cases where experimental data already exist.

In this article we propose to compute thermal conductivity of pure gases and their mixtures on the basis of such relations[4] and the necessary experimental data. Wherever necessary an effort has also been made to check such relations on the basis of existing experimental data.

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INTER RELATIONS BETWEEN THERMAL CONDUCTIVITY AND OTHER TRASPORT PROPERTIES

The working relations differ considerably depending upon whether the involved gases are all monoatomic or are also polyatomic. We consider first monoatomic gases and their mixtures and then other complicated systems involving polyatomic gases. The Chapman-Enskog expression for the thermal conductivity of a pure monoatomic gas i, λ°_i, is[5,6]

$$\lambda^\circ_i = \frac{75\,R}{64\,N}\left(\frac{RT}{\pi M_i}\right)^{\frac{1}{2}} \frac{f_\lambda}{\sigma_{ii}{}^2\,\Omega_{ii}{}^{(2,2)*}}, \qquad (1)$$

where R is the gas constant per mole, N is Avogadro's number, M_i is the molecular weight of the pure gas i, T is the absolute temperature, σ_{ii} is the molecular diameter, and $\Omega_{ii}{}^{(2,2)*}$ is a reduced Chapman-Cowling Collision integral. f_λ is a small correction factor and arises due to higher approximations. It is fairly insensitive to the temperature variations and nature of the gas and its value seldom departs from unity by any appreciable amount.

Similarly, the diffusion coefficient for the pure component i, D_{ii}, is given by[5,6]

$$D_{ii} = [D_{ii}]_1\; f_D, \qquad (2)$$

where

$$[D_{ii}]_1 = \frac{3\,RT}{8\,Np}\left(\frac{RT}{\pi M_i}\right)^{\frac{1}{2}} \frac{1}{\sigma_{ii}{}^2\,\Omega_{ii}{}^{(1,1)*}}. \qquad (3)$$

Here p is the pressure in dyne cm.$^{-2}$ and f_D is a correction factor which behaves very similar to f_λ.

The coefficient of viscosity, η_i, is given by[5,6]

$$\eta_i = \frac{5}{16}\left(\frac{M_i\;RT}{\pi}\right)^{\frac{1}{2}} \frac{f_\eta}{\sigma_{ii}{}^2\,\Omega_{ii}{}^{(2,2)*}}. \qquad (4)$$

It is now possible to correlate Eqs. (1) & (2) and derive the following inter-relation between thermal conductivity and Diffusion:

$$\lambda^\circ_i = \frac{25\,p}{8\,T} \cdot \frac{f_\lambda}{A^*_{ii}\,f_D} \cdot D_{ii}, \qquad (5)$$

where A_{ii}^* is a demensionless quantity, being the ratio of the two collision integrals $\Omega_{ii}{}^{(2,2)*}$ and $\Omega_{ii}{}^{(1,1)*}$. It has a weak dependence on the temperature and the inter-molecular potential and is usually approximated by a constant value with fair accuracy[6,1]. f_λ and f_D have also a similar character and their ratio can again be taken as unity to a high degree of accuracy. Keeping in view the uncertainties associated with λ and D, one can assign these constants the values, $A_{ii}^* = 1{\cdot}10$ and $f_\lambda = f_D$. Thus, we rewrite the inter-relation of Eq. (5) in the following simple form and assume it to have good accuracy[1]:

$$\lambda^\circ_i = \frac{25\,p}{8{\cdot}8\,T}\,D_{ii}. \qquad (6)$$

Similarly one can combine thermal conductivity and viscosity coefficients as given by Eqs. (1) and (4) respectively. The final inter-relation is

$$\lambda^\circ_i = \frac{15R}{M}\,\eta_i \qquad (7)$$

Relation (7) is somewhat preferable to relation (6) for two reasons. Firstly η_i values are determined with much greater accuracy than D_{ii} values. Secondly, the quantity like A_{ii}^* does not appear at all, though the approximation of assuming the ratio (f_λ/f_η) equal to unity is involved but it should cause no anxiety because of its reasonbaly good validity.

For mixtures of monoatomic gases the theoretical expression for thermal conductivity, λ°_{mix}, is given by[7,8]

$$\lambda^\circ_{mix} = 4 \begin{vmatrix} L_{11} \cdots\cdots L_{1n} & x_1 \\ 1 \quad\quad 1 & 1 \\ 1 \quad\quad 1 & 1 \\ 1 \quad\quad 1 & 1 \\ 1 \quad\quad 1 & 1 \\ L_{n1} \cdots\cdots L_{nn} & x_n \\ x_1 \cdots\cdots x_n & 0 \end{vmatrix} \div \begin{vmatrix} L_{11} \cdots\cdots L_{1n} \\ 1 \quad\quad 1 \\ 1 \quad\quad 1 \\ 1 \quad\quad 1 \\ 1 \quad\quad 1 \\ L_{n1} \cdots\cdots L_{nn} \end{vmatrix} \tag{8}$$

Here

$$L_{ii} = -\frac{4\,x_i^2}{\lambda_i} - \frac{16\,T}{25\,p} \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{x_i\,x_k}{D_{ik}} \left[\frac{7\cdot50\,M^2_i + 6\cdot25\,M^2_k + 4\,M_i\,M_k\,A^*_{ik} - 3\,M^2_k\,B^*_{ik}}{(M_i + M_k)^2}\right] \tag{9}$$

and

$$L_{ij}\,(i \neq j) = \frac{16\,T}{25\,p}\,\frac{x_i\,x_j}{D_{ij}} \left[\frac{M_i\,M_j\left(\frac{55}{4} - 3B^*_{ij} - 4\,A^*_{ij}\right)}{(M_i + M_j)^2}\right], \tag{10}$$

n is the number of components in the mixture and x_i is the molefraction of the i-th component. B^*_{ik} is again a dimensionless quantity similar to A^*_{ik}. Equations (9) and (10) are further simplified by putting $A^*_{ik} = B^*_{ik} = 1\cdot10$. Thus, one can calculate λ°_{mix} from Eq. (8) if the pure λ_i and D_{ij} values be known[1]. We employ this procedure for predicting λ_{mix} values where D_{ij} values are known.

For pure polyatomic gases four different theories are already known and consequently an equal number of interrelations are possible. Mathur and Saxena[4] have discussed these different relations and their accuracies. We employ here the relation obtained on the basis of Hirschfelder's theory[9] inview of its simplicity and accuracy. We finally have[4], for the thermal conductivity of the pure polyatomic gas i, λ_i as

$$\lambda_i = f_H \cdot \lambda^\circ_i\,, \tag{11}$$

where

$$f_H = 0\cdot115 + 0\cdot354\,\frac{\gamma}{\gamma - 1} \tag{12}$$

γ is the familiar ratio of the specific heat at constant pressure to that at constant volume.

Similarly for mixtures we consider only the expression given by Hirschfelder[10] but report only the final result in brief as the details are given in an earlier paper[4]. We have

$$\lambda_{mix} = \lambda^\circ_{mix} + \sum_{i=1}^{n} \frac{\lambda_i - \lambda^\circ_i}{1 + \sum\limits_{\substack{j=1 \\ j \neq i}}^{n} \frac{D_{ii}}{D_{ij}}\,\frac{x_j}{x_i}} \tag{13}$$

λ°_{mix} and λ°_{i} can be obtained according to Eqs. (8) and (7) respectively. Further D_{ii} can be generated from the following relation, which is readily obtained by combining Eqs. (6) and (7), :

$$D_{ii} = 1 \cdot 32 \, \frac{R}{M_i} \, \frac{T}{p} \, \eta_i \quad . \tag{14}$$

Thus, if D_{ij} and λ_i be known experimentally λ_{mix} can be determined from Eq. (13).

In order tc predict the different transport properties on the basis of different correlations developed and described in the previous section, one requires a large body of reliable experimental data. A large number of workers have reported such data under different experimental conditions and these required to be pooled tcgether cleverly and a best set of values to be evolved. In a few cases such review works are fortunately available and we present references to different data along with the best compromised set in this section for use in the prediction of properties.

The experimental data on the viscosity of pure gases viz., He, Ne, Ar, Kr, Xe, H_2, O_2, N_2, air, CO, CO_2 and CH_4 at different temperatures have been reported[11–25]. All

TABLE 1

RECORD OF η AND D DATA FOR PURE GASES AS A FUNCTION OF TEMPERATURE EMPLOYED IN CALCULATION AND OBTAINED BY SMOOTHING THE AVAILABLE EXPERIMENTAL DATA

Temp. °K	$\eta \times 10^7$ gm. cm.$^{-1}$ sec.$^{-1}$					D cm.^{2} sec.$^{-1}$				
	He	*Ne*	*Ar*	*Kr*	*Xe*	*He*	*Ne*	*Ar*	*Kr*	*Xe*
80	821	1198	688			0·198	0·0513	0·0140		
120	1068	1646	993			0·367	0·101	0·0310		
160	1290	2026	1298			0·585	0·175	0·0555		
200	1496	2376	1594			0·837	0·263	0·086		0·0267
240	1692	2708	1878			1·125	0·365	0·122		..
250	..	..	..			..	..	..		0·040
273·2	..	..	..	2334		..	..	..	0·084	..
280	1888	3021	2145	..		1·433	0·470	0·162	..	..
283·2	..	..	..	2405		..	..	..	0·091	..
289·5	..	..	..	2459		..	..	..	0·095	..
296	1970	..	..	..		1·560	..	..	..	..
300	1987	..	2260	..	2300		..	..	..	0·0575
320	..	3313	2403	..	..		0·588	0·208	..	..
350	..	3500	2573	..	2630		0·690	0·244	..	..
373·2	..	..	..	3609	..				0·165	0·0777
375	..	..	..		2820					0·0885
400	..	3810	..		3009					
450	..	..	..		3351					
500	..	4380	3330		3652					
550	..	..	..		3954					
600	3186	..	..							
800	..	5918	4590							
900	4158	..	..							
1000	..	6800	5305							
1100	4745		..							
1200			5947							
1400			6525							
1600			7060							
1800			7560							
2000			8037							
2073			8200							

these data were plotted on a large graph paper for an individual gas as a function of temperature and values read at the round temperatures in each case. These smooth values for the five rare gases are recorded in Table 3, while for the seven polyatomic gases in Table 9. Most of the data are consistent within one percent, save in a few cases the maximum deviation goes upto two to three percent. In the case of air the deviation which goes upto three percent, may very well be due to the different compositions of the air sample employed.

The data of the self diffusion coefficient of the pure rare gases which are available are of : Bendt[26] for *He*, Winn[27] for *Ne* and *Ar*, Amdur and Schatzki[28] for *Xe* and Wendt et al.[29] for *Kr*. The smooth values for these gases at the desired temperature are reported in Table 3 and are consistent within a margin of one to two percent. The data for binary diffusion coefficients of rare gases of different workers [28], [30–38] after being smooth are reproduced in Table 5. The scatter of the experimental points from the smooth curve is appreciable in many cases and ranges between the maximum limit of twelve percent to the minimum of two percent on the average, the percentage deviation is four percent. The data for the binary diffusion coefficients involving polyatomic gases are reported in

TABLE 2

RECORD OF EXPERIMENTAL DATA OF η AND D_{12} AND D_{ii} AS GENERATED FROM η DATA

Gas-pair	Temp. °K	$\lambda_1 \times 10^5$ cal. cm.$^{-1}$ sec.$^{-1}$deg.$^{-1}$	$\lambda_2 \times 10^5$ cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$	$\eta_1 \times 10^5$ gm. cm.$^{-1}$ sec.$^{-1}$	$\eta_2 \times 10^5$ gm. cm.$^{-1}$ sec.$^{-1}$	D_{12} cm.^{2} sec.$^{-1}$	D_{11}	D_{22}
N_2—He	300	6·10	36·99	17·86	19·87	0·743	0·207	
	600	10·47	59·31	29·20	31·86	2·400	0·680	
	900	14·13	77·40	37·68	41·58	4·760	1·282	
	1100	16·17	88·32	42·22	47·45	6·686	1·796	
H_2—Ar	300	4·22	42·80	22·60	8·96	0·87	—	1·444
	500	6·21	63·70	33·20	12·55	2·13	—	3·372
	800	8·56	85·75	45·90	17·30	4·98	—	7·437
	1000	9·89	102·0	53·05	20·05	7·33	—	10·774
CO_2—O_2	300	3·90	6·37	14·95	20·71	0·161	0·110	0·210
	500	7·73	9·73	23·75	30·10	0·419	0·292	0·509
	800	13·30	14·30	34·00	41·40	0·9696	0·669	1·121
	1000	16·30	17·10	39·55	47·55	1·43	0·973	1·610
CO_2—N_2	300	3·90	6·10	14·95	17·86	0·173	0·110	0·207
	600	9·83	10·47	27·50	29·20	0·605	0·406	0·680
	900	14·85	14·13	36·85	37·68	1·217	0·816	1·282
	1100	17·83	16·17	44·65	42·22	1·702	1·142	1·796
CO_2—Air	400	5·70	7·85	19·50	23·00	0·273	0·192	0·346
	600	9·83	10·80	27·50	30·38	0·555	0·406	0·686
	800	13·30	13·55	34·00	36·60	0·915	0·669	1·083
	1000	16·30	15·93	39·55	42·00	1·32	0·973	1·580
O_2—H_2	300	6·37	42·80	20·71	8·96	0·821	0·210	1·444
	500	9·73	63·70	30·10	12·55	2·090	0·509	3·372
	800	14·30	85·75	41·40	17·30	4·748	1·121	7·437
	1000	17·10	102·0	47·55	20·05	6·930	1·610	10·774
O_2—CO	300	6·37	6·03	20·71	17·85	0·224	0·210	0·207
	500	9·73	9·10	30·10	26·08	0·542	0·509	0·504
	800	14·30	13·15	41·40	35·29	1·195	1·121	1·092
	1000	17·10	15·45	47·55	40·40	1·73	1·610	1·563
O_2—CH_4	300	6·37	8·27	20·71	11·16	0·226	0·210	0·226
	500	9·73	15·73	30·10	16·80	0·581	0·509	0·567
	800	14·30	28·20	41·40	23·24	1·3268	1·121	1·255

TABLE 3

SMOOTH EXPERIMENTAL λ AND D_{12} VALUES EMPLOYED IN THE PREDICTION OF λ° *mix* FOR MONOATOMIC GAS MIXTURES

Gas-pair	Temp °K	$\lambda_1 \times 10^5$ cal cm^{-1} sec^{-1} deg^{-1}	$\lambda_2 \times 10^5$ cal cm^{-1} sec^{-1} deg^{-1}	D_{12} cm^2 sec^{-1}
He—Ne	315	12·00	27·4	1·138
He—Kr	315	2·36	37·4	0·700
He—Xe	300	1·43	36·3	0·556
	390	1·79	42·9	0·866
Ne—Ar	300	4·24	11·6	0·320
	470	6·05	15·9	0·720
Ne—Kr	315	2·36	12·0	0·284
Ne—Xe	315	1·48	12·0	0·238
Ar—Kr	300	2·27	4·24	0·145
	470	3·38	6·05	0·323
Ar—Xe	300	1·43	4·24	0·112
	390	1·79	5·27	0·189

Note Subscript 1 refers to the heavier component.

TABLE 4

COMPARISON OF DIRECTLY MEASURED AND INDIRECTLY GENERATED VALUES OF λ° FROM D AND η FOR PURE GASES AS A FUNCTION OF TEMPERATURE

Gas	Temp. °K	$\lambda^\circ \times 10^5$ (cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$) Exptl.	from D	% Dev.	from η	% Dev.
Ar	80	1·24	1·20	—3·2	1·28	+3·2
	120	1·88	1·78	—5·3	1·85	—1·6
	160	2·46	2·39	—2·8	2·42	—1·6
	200	3·01	2·96	—1·7	2·97	—1·3
	240	3·53	3·50	—0·8	3·50	—0·8
	280	4·04	3·98	—1·5	4·00	—1·0
	320	4·48	4·47	—0·2	4·48	0·0
	350	4·82	4·79	—0·6	4·80	—0·4
Ne	80	4·50	4·41	—2·0	4·42	—1·8
	120	6·00	5·79	—3·5	6·08	+1·3
	160	7·30	7·52	+3·0	7·48	+2·5
	200	8·60	9·04	+5·1	8·77	+2·0
	240	9·90	10·50	+6·1	10·00	+1·0
	280	11·10	11·50	+3·6	11·20	+0·9
	320	12·30	12·60	+2·4	12·20	—0·8
	350	13·00	13·60	+4·6	12·90	—0·8
He	80	15·30	17·00	+11·1	15·30	0·0
	120	19·60	21·00	+7·1	19·90	+1·5
	160	23·80	25·10	+5·5	24·00	+0·8
	200	27·80	28·80	+3·6	27·90	+0·3
	240	31·50	32·20	+2·2	31·50	0·0
	280	34·80	35·20	+1·1	34·80	0·0
	296	36·00	36·30	+0·8	36·30	+0·8
Kr	273·2	2·04	2·11	+3·4	2·08	+2·0
	283·8	2·12	2·21	+4·2	2·14	+0·9
	289·5	2·16	2·26	+4·6	2·19	+1·4
	373·2	2·78	3·04	+9·4	3·21	+15·5
Xe	200	0·94	0·92	—2·1	..	..
	250	1·20	1·10	—8·3	..	..
	300	1·43	1·32	—7·7	1·31	—8·4
	350	1·64	1·53	—6·7	1·49	—9·1
	375	1·72	1·62	—5·8	1·60	—7·0

Table 9. These are by Walker and Westenberg[39] for N_2-He, CO_2-N_2, CO_2-O_2, O_2-H_2, O_2-CH_4 and O_2-CO systems. The other data belong to Klibanova, Pomerantsev, and Frank-Kamenetsku[40]. for CO_2—*air*, Westenberg and Frazer[41] for H_2-Ar, and Weissman and Mason[42] for N_2-O_2. The last data are generated from the corresponding viscosity data. Smoothed values for all the systems are reported in Table 9 and are of enough good internal consistency, usually of the order of one to two percent.

The available experimental thermal conductivity data on pure gases have already been reviewed by Gandhi & Saxena[43] for rare gases and Gambhir & Saxena[44] for non-polar polyatomic gases. These are reproduced at the desired temperatures in Tables 1, 2, 5, 6 and 9. For air we have used the data of Bromley[45]. To give an idea of the consistency of these data we may add that it is about two percent at lower temperatures and shoots to about five percent at higher temperatures.

The ratio of the two specific heats of gases at constant pressure and volume, α, are also needed for different gases and these have been taken from International Critical Table[46]. We have interpolated the values at the desired temperatures and these are listed in Tables 6 and 7 and are of good internal consistency.

The indirectly generated values of thermal conductivity have also been compared with the directly observed values wherever possible. In this connection the data of Srivastava & Srivastava[47] for H_2-Ar, Barua[48], Cheung, Bromley & Wilke[49] for N_2-He, Cheung et al[49] for O_2-CO_2, Westenberg & De-Hass[50], Keyes[5'], and Rothman[51] for N_2-CO_2 are employed. All these data were plotted as a function of composition and values read at the desired compositions. These are also of reasonable accuracy and a

TABLE 5

COMPARISON OF DIRECTLY MEASURED AND INDIRECTLY GENERATED VALUES OF λ° FROM η FOR PURE GASES AS A FUNCTION OF TEMPERATURE

Gas	Temp. °K	$\lambda^\circ \times 10^5$ (cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$)		%Dev.
		Exptl.	Generated	
He	300	36·3	36·99	+1·9
	600	58·0	59·31	+2·3
	900		77·40	
	1100		88·33	
Ne	400	14·3	14·06	—1·7
	500	16·4	16·17	—1·4
	800	22·0	21·84	—0·7
	1000		25·10	
Ar	300	4·25	4·22	—0·7
	500	6·34	6·21	—2·1
	800	8·90	8·56	—3·8
	1000		9·89	
	1200		11·09	
	1400		12·17	
	1600		13·17	
	1800		14·10	
	2000		14·99	
	2073		15·29	
Xe	400	1·82	1·71	—6·0
	450	2·00	1·90	—5·0
	500	2·18	2·07	—5·0
	550	2·36	2·25	—4·7

good assessment of the consistency is possible from the detailed work of Saxena, Mathur & Gupta[53].

We also consider the thermal conductivity data on the ternary system $N_2 - O_2 - CO_2$ of Cheung, Bromley & Wilke [49] and these are reported in Table 11.

RESULTS AND DISCUSSIONS

Employing the simple inter-relations for $\lambda°$ as given by Eqs. (6) and (7) in terms of diffusion and viscosity coefficients respectively, we first generate the $\lambda°$ values as a function of temperature. These are recorded in Table 1 for the five rare gases in columns 4 and 6. In this Table only those temperatures are considered where the directly measured values are available and these are listed in this very table in column 3. To facilitate

TABLE 6

VALUES OF GENERATED λ FOR POLYATOMIC GASES AS A FUNCTION OF TEMPERATURE AND THEIR COMPARISON WITH THE EXPERIMENTAL λ VALUES. VALUES OF γ AND GENERATED $\lambda°$ ARE ALSO REPORTED*.

Gas	Temp °K	$\lambda \times 10^5$ Exptl. (1)	γ (2)	$\lambda° \times 10^5$ (3)	$\lambda \times 10^5$ Generated (4)	% Dev. of (4) over (1)
CO_2	300	3·90	1·301	2·53	4·16	+6·7
	400	5·70	1·276	3·30	5·78	+1·4
	500	7·73	1·258	4·02	7·39	—4·4
	600	9·83	1·244	4·66	8·95	—9·0
	800	13·30	1·223	5·76	11·86	—10·8
	900	14·85	1·215	6·24	13·20	—11·1
	1000	16·30	1·208	6·70	14·52	—10·9
	1100	17·83	1·203	7.14	15·80	—11·4
O_2	300	6·37	1·401	4·82	6·51	+2·2
	500	9·73	1·395	7·01	9·56	—1·7
	800	14·30	1·386	9·64	13·37	—6·5
	1000	17·10	1·378	11·07	15·56	—9·0
N_2	300	6·10	1·401	4·75	6·42	+5·2
	600	10·47	1·392	7·76	10·64	+1·6
	900	14·13	1·382	10·02	13·99	—1·0
	1100	16·17	1·374	11·23	15·90	—1·7
H_2	300	42·80	1·408	33·11	44·23	+3·3
	500	63·70	1·397	46·38	63·12	—0·9
	800	85·75	1·380	63·93	89·50	+4·4
	1000	102·00	1·371	74·10	105·50	+3·4
CO	300	6·03	1·401	4·75	6·41	+6·3
	500	9·10	1·395	6·94	9·47	+4·1
	800	13·15	1·386	9·39	13·02	—1·0
	1000	15·45	1·378	10·75	15·11	—2·2
CH_4	300	8·27	1·281 (1·310)	5·18	8·96 (8·34)	+8·3 (+0·8)
	500	15·73	1·179 (1·213)	7·80	19·13 (16·62)	+21·6 (+5·7)
	800	28·20	1·121 (1·152)	10·79	36·63 (30·19)	+30·0 (+6·7)
Air	400	7·85	1·400	5·95	8·05	+2·5
	600	10·80	1·395	7·86	10·73	—0·6
	800	13·53	1·388	9·47	13·07	—3·5
	1000	15·93	1·380	10·86	15·23	—4·4

*The values of γ within braces are obtained according to the formula given by Kaye & Laby, Tables of Physical and Chemical Constants, p. 154, 1958, Published by Longmans.

the comparison of the two sets of indirectly generated $\lambda°$ values with the directly measured values we report in columns 5 and 7 the percentage deviations. On the whole we find that the viscosity generated $\lambda°$ values are somewhat better. The absolute average deviations for the gases, *Ar*, *Ne*, *He*, *Kr* and *Xe* are 1·2, 1·4, 0·5, 5·0 and 8·2% respectively for viscosity and 2·0, 3·8, 4·5, 5·4 and 6·1% respectively for diffusion. The relatively inferior agreement for *Xe* and for *Kr* at the highest temperature is due to the poor and in-accurate experimental data. We thus conclude that if there is a choice, generation of $\lambda°$ from viscosity data is preferable. This is understandable for viscosity measurements are possible with much higher accuracy than diffusion measurements. This is also a happy coincidence for viscosity data are available over a much wider temperature range than the diffusion coefficients. Taking advantage of these circumstances we compute the $\lambda°$ values for *He*, *Ne*, *Ar* and *Xe* using their high temperature available viscosity data. These are reported in Table 2 wherein we also list in columns 3 and 5 the available experimental values and the percentage deviation of the computed values from the corresponding experimental quantities respectively. Here again we find that the generated values are satisfactory and *Xe* seems to be a serious exception. We feel that this is because of the relatively poorer accuracy of the experimental data for this gas and which we suggest should be measured with great care and accuracy.

We next consider the possibility of generating $\lambda°_{mix}$ for binary rare gas mixtures according to the previously described procedure and Eqs. (8) to (10). The reliability of such an approach has already been established by the work of Gandhi and Saxena[1]. In

TABLE 7

VALUES OF GENERATED λ FOR POLYATOMIC GASES AT HIGH TEMPERATURES. η, γ AND $\lambda°$ VALUES ARE ALSO RECORDED*

Gas	Temp °K	$\eta \times 10^5$ gm cm^{-1} sec^{-1}	γ	$\lambda° \times 10^5$ cal cm.$^{-1}$ sec.$^{-1}$ deg^{-1}	$\lambda \times 10^5$ cal. cm.$^{-1}$ sec.$^{-1}$ deg^{-1}
CO_2	1200	44·53	1·198	7·54	16·13
		47·66		8·07	16·27
	1500	51·39	1·189	8·70	19·41
		55·29		9·36	20·89
O_2	1200	54·92	1·369	12·79	16·79
	1500	62·64	1·352	14·58	19·84
N_2	1200	44·52	1·369	11·84	15·54
		46·13		12·67	16·64
	1500	50·50	1·352	13·43	18·27
		52·47		13·95	18·98
H_2	1200	22·05	1·362	81·49	108·62
	1500	24·96	1·348	92·24	126·49
CO	1200	44·96	1·369	11·96	15·70
	1500	51·09	1·352	13·59	18·49
CH_4	1000	26·95	(1·131)	12·51	39·67
		28·06		13·03	41·32
	1200	30·25	(1·118)	14·05	48·74
		31·51		14·63	50·75
	1500	34·67	(1·106)	16·10	61·32
		36·12		16·77	63·88
Air	1200	46·42	1·370	12·01	15·75
	1500	53·10	1·352	13·74	18·69

*The values of γ within braces are obtained according to the formula given by Kaye & Laby, Tables of Physical and Chemical Constants, p. 154, 1958, Published by Longmans,

Table 4 we report predicted λ°_{mix} values for eight different binary gas pairs at a particular temperature for three arbitrarily chosen compositions. The scope of such calculations is really limited by the scope and availability of diffusion data. Unfortunately, such data are not available over an enough extended temperature range. Till then we will suggest that for practical needs one might employ the available binary viscosity data to generate diffusion data and there after the λ°_{mix} values according to the procedure outlined above. It may be pointed out that all the reliable data required in connection with the calculations of Table 4 are reproduced in Table 5.

We have suggested the possibility of generating λ of pure polyatomic gases on the basis of Eqs. (11) and (12). Now we report and discuss the values generated according to this procedure. Such results are reported in Table 6 and 7. In the former we consider those gases and at such temperatures where the directly measured λ values are available to warrant a direct check of theory and experiment. Thus, in Table 6 column 3 we list the directly measured experimental values, λ° generated from η values (reported in Table 9), and generated λ values finally in column 6. The latter calculation requires the γ values and these are also recorded in column 4 of this very table. In the last column to make the comparison of measured and generated λ values somewhat straightforward we list the percentage deviation between the two sets. We find that this method works well for O_2, N_2, air H_2, and CO. The average absolute deviations for these gases being 4·9, 2·4, 2·8, 3·0 and 3·4 percent respectively. For CO_2 and CH_4 the deviations are somewhat pronounced. The actual average magnitude being 8·2 and 20·0 percent respectively. It seems that this procedure is alright for simple diatomic gases for which Hirschfelder's theory[9] approximates the facts rather satisfactorily. For polyatomic molecules more sophisticated theories[54, 55] are needed. In Table 7 for these very seven gases we report the similarly generated λ values at somewhat higher temperatures where η and γ values are known. In a few cases two sets of values are available and in such cases two sets of λ values are also given. We hope that these λ values will be of some use in the design problems in the absence of directly computed values.

Prediction of thermal conductivity of mixtures involving polyatomic gases is possible on the basis of Eqs. (13) and (14). A large body of initial input information is needed for such a correlation. Luckily, it turns out that such calculations are possible for many systems and we report the results here for eight systems. All the necessary information is included in Table 9. The computed λ_{mix} values are given in Table 8 and provide valuable

TABLE 8

PREDICTED λ°_{mix} VALUES OF MONOATOMIC GAS MIXTURES AS A FUNCTION OF COMPOSITION

Gas-pair	Temp. °K	λ° *mix* × 10^5		
		$x_1=0\cdot25$	$x_1=0\cdot50$	$x_1=0\cdot75$
He—Ne	315	27·11	20·18	15·36
He—Kr	315	19·28	10·67	5·65
He—Xe	300	16·91	8·76	4·27
	390	20·16	10·51	5·17
Ne—Ar	300	8·93	6·96	5·44
	470	12·32	9·68	7·65
Ne—Kr	315	7·78	5·25	3·56
Ne—Xe	315	6·82	4·16	2·55
Ar—Kr	300	3·61	3·09	2·65
	470	5·16	4·44	3·85
Ar—Xe	300	3·07	2·31	1·79
	390	3·89	2·95	2·28

NOTE—x_1 refers to the mole-fraction of the heavier component.

alternatives in the absence of measured values. For four of these systems directly measured values are also available. These we employ to have an idea of the degree of reliance which we should associate with the values reported in Table 8. This work is reported in Table 5 and includes H_2—Ar, He—N_2, O_2—CO_2 and N_2—CO_2 systems. The directly measured values for these systems were read at the round compositions of 0·25, 0·50 and 0·75. On the other hand the generated values of λ_{mix} were interpolated at the necessary temperature of Table 10. Thus the point to point comparison became possible. In the last 6th column of Table 10 we report the percentage deviations between the generated and measured values. It is gratifying to note that the agreement is invariably good except for the H_2—Ar system. The average absolute deviations are 8·8% for H_2—Ar, 3·1% for N_2—He, 1·6% for O_2—CO_2 and 2·3% for N_2—CO_2. This all should be regarded as completely satisfactory and very promising in view of the fact that the data for H_2—Ar are doubtful. This has been earlier mentioned by us[53] and has since been confirmed by actual measurements on this system by Gupta and Saxena (in course of publication). Thus, we suggest this procedure as a potential possibility for estimating λ_{mix} values.

TABLE 9

PREDICTED λ_{mix} VALUES AS A FUNCTION OF TEMPERATURE AND COMPOSITION

Gas-pair	Temp °K	$\lambda_{mix} \times 10^5$ (cal cm^{-1} sec^{-1} deg^{-1})		
		x_1=0·25	x_1=0·50	x_1=0·75
N_2—He	300	22·31	14·35	9·46
	600	36·23	24·18	15·81
	900	47·91	31·55	21·22
	1100	54·96	36·26	24·37
H_2—Ar	300	27·16	16·91	9·65
	500	41·28	25·73	15·41
	800	56·86	36·25	20·42
	1000	68·06	43·46	25·87
CO_2—O_2	300	5·69	5·05	4·53
	500	9·39	8·90	8·34
	800	14·60	14·44	13·97
	1000	17·74	17·68	17·15
CO_2—N_2	300	5·65	5·11	4·23
	600	10·80	10·73	10·37
	900	15·23	15·59	15·41
	1100	17·75	18·40	18·37
CO_2—Air	400	7·30	6·75	6·21
	600	10·66	10·43	10·15
	800	13·76	13·75	13·59
	1000	16·36	16·52	16·48
O_2—H_2	300	27·45	17·90	11·23
	500	42·84	28·35	17·78
	800	58·93	39·67	25·35
	1000	70·61	47·68	30·47
O_2—CO	300	6·27	6·41	6·44
	500	9·48	9·71	9·80
	800	13·80	14·22	14·39
	1000	16·35	16·95	17·23
O_2—CH_4	300	7·69	7·17	6·72
	500	14·27	12·77	11·25
	800	25·09	21·73	18·06

NOTE—x_1 refers to more-fraction of the heavier component.

TABLE 10

COMPARISON OF PREDICTED AND EXPERIMENTAL λ_{mix} VALUES

Gas-pair	Temp. °K	X_1	λ Exptl. cal. cm.$^{-1}$ sec.$^{-1}$ deg^{-1}	λ Pred. cal. cm^{-1} sec.$^{-1}$ deg^{-1}	Dev. %
H_2—Ar	311·2	0·25	25·3	28·1	+11·1
		0·50	15·9	17·3	+8·8
		0·75	9·4	10·0	+6·4
He—N_2	303·2	0·25	21·7	22·4	+3·2
		0·50	13·9	14·3	+2·9
		0·75	8·9	9·5	+6·7
	318·2	0·25	22·5	23·2	+3·1
		0·50	14·4	14·9	+3·5
		0·75	9·4	9·9	+5·3
	377·2	0·25	25·9	25·9	0·0
		0·50	16·8	16·7	—0·6
		0·75	11·1	11·2	+0·9
	589·2	0·25	34·1	35·6	+4·4
		0·50	22·5	23·00	+2·2
		0·75	14·8	15·5	+4·7
O_2—CO_2	370·2	0·25	6·95	7·00	+0·7
		0·50	6·30	6·40	+1·6
		0·75	5·73	5·87	+2·4
N_2—CO_2	300·0	0·25	5·25	5·65	+7·6
		0·50	4·90	5·11	+4·3
		0·75	4·30	4·23	—1·6
	323·2	0·25	5·90	6·03	+2·2
		0·50	5·27	5·55	+5·3
		0·75	4·80	4·73	—1·5
	423·2	0·25	7·80	7·75	—0·6
		0·50	7·30	7·40	+1·4
		0·75	6·85	6·87	+0·3
	500·0	0·25	8·90	9·05	+1·7
		0·50	8·75	8·85	+1·1
		0·75	8·20	8·43	+2·8
	523·2	0·25	9·50	9·47	—0·3
		0·50	9·13	9·30	+1·9
		0·75	8·75	8·90	+1·7
	623·2	0·25	11·3	11·2	—0·9
		0·50	11·2	11·1	—0·9
		0·75	11·0	10·8	—1·8
	745·2	0·25	12·5	13·0	+4·0
		0·50	12·5	13·2	+5·6
		0·75	12·4	12·9	+4·0
	846·2	0·25	14·1	14·5	+2·8
		0·50	14·2	14·8	+4·2
		0·75	14·0	14·6	+4·3
	950·2	0·25	16·0	16·0	0·0
		0·50	16·3	16·4	+0·6
		0·75	16·2	16·2	0·0
	1000·0	0·25	16·4	16·6	+1·2
		0·50	17·1	17·1	0·0
		0·75	16·3	16·9	—3·7
	1047·2	0·25	17·8	17·2	—3·4
		0·50	18·3	17·8	—2·7
		0·75	18·3	17·7	—3·3

Note—X_1 refers to mole-fraction of the heaviest component.

TABLE 11

COMPARISON OF EXPERIMENTAL AND PREDICTED λmix VALUES FOR THE TERNARY MIXTURE N_2—O_2—CO_2 at 97° C. THE CONCENTRATIONS ARE $x\ (CO_2) = 0 \cdot 3040$, $x\ (O_2) = 0 \cdot 3729$ AND $x\ (N_2) = 0 \cdot 3231$.

λ_1	λ_2	λ_3	λ Exptl.	λ Pred.	%Dev.
5·218	7·660	7·331	6·729	6·787	+0·9

TABLE 12

RECORD OF GENERATED SELF DIFFUSION AND FROZEN THERMAL CONDUCTIVITY VALUES FROM VISCOSITY DATA AND THE EXPERIMENTAL BINARY DIFFUSION VALUES USED TO PREDICT λ *mix* FOR TERNARY SYSTEM N_2—O_2—CO_2 at 97°C.

D_{11}	D_{22}	D_{33}	λ°_1	λ°_2	λ°_3	D_{12}	D_{2}	D_{31}
0·165	0·304	0·298	3·07	5·66	5·54	0·234	0·300	0·256

Measurements on multicomponent thermal conductivity are relatively rare and we hope that a general programme cannot respond to the needs also. The reason is obvious that there can be a large number of systems of all possible choices for the components and then their relative proportions. It should not be regarded as very disappointing for if the validity of the relation (Eq. 13) is established for multicomponent systems, the computation of λ_{mix} will be a straight-forward job. We explore this possibility by considering the system N_2—O_2—CO_2 for which all the relevant information is available. In Table 11 we report the directly measured and indirectly generated value. It is encouraging to see the excellent agreement between the two sets of values. All the other necessary data needed in this calculation are reproduced in Table 12. We on the basis of this calculation and the ones reported by Gandhi and Saxena[1] on the ternary systems of rare gases suggest the exploitation of the outlined method for estimating the multicomponent thermal conductivity values.

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