CALCULATION OF THERMAL CONDUCTIVITY OF POLYATOMIC GAS MIXTURES AT HIGH TEMPERATURES

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Reliable methods for prediction of thermal conductivity at high temperatures are very useful for a variety of important practical needs. Three different methods (*i*) approximate (*ii*) semitheoretical and (*iii*) empirical have been investigated. The success of these procedures is demonstrated by actual computation for a large number of systems at temperatures and compositions where direct measurements are available. These procedures are valuable as the rigorous theory besides being complicated requires a large amount of input information and even then leads to unreliable values.

The theory of thermal conduction in polyatomic gases and gas mixtures is very little understood at the moment. Hirschfelder made the first significant contribution in this direction and developed a semiclassical theory for pure gases[1] as well as multicomponent mixtures[2]. The theory for mixtures being complicated has been simplified by Mason and Saxena[3] under well defined approximations. The theory for pure gases has also been given by Mason and Monchick[4] who based the development on the kinetic theory expression of polyatomic gases. Saxena, *et al*[5]. improved the theory of Hirschfelder[1] by taking into account the translational-internal energy exchnage. For mixtures also Monchick, *et al*[6] have developed a formal kinetic theory but the results are not in a form where they may be used for actual calculations. Saxena, *et al*[7] have consequently improved the Hirschfelder's expression[2] for mixtures in the same way as for pure gases. The calculations on all these theories [4,5,7] require a large amount of information which is not always available. Therefore simpler relations with even moderate reliance will be of great value for a vast number of practical needs of design engineers. Three different methods are discussed here and then their worth assessed by applying them for a large number of systems where directly measured values are available. This work will thus enable further prediction at higher temperatures with some idea of their reliability.

METHODS

Approximate method—Mason & Saxena[3] have shown that the coefficient of thermal conductivity λ_{mix} of a n-component system is given by

$$\lambda_{mix} = \sum_{i=1}^{n} \lambda_i \left[1 + \sum_{\substack{j=1 \\ j \neq i}}^{n} \varphi_{ij} \frac{x_j}{x_i}\right]^{-1} \qquad (1)$$

Here λ_i is the thermal conductivity of the pure i th component, x_i is the mole fraction of the ith component and φ_{ij} is defined as

$$\varphi_{ij} = \frac{1{\cdot}065}{2\sqrt{2}} \left(1 + \frac{M_i}{M_j}\right)^{-\frac{1}{2}} \left[1 + \left(\frac{\lambda^\circ_i}{\lambda^\circ_j}\right)^{\frac{1}{2}} \left(\frac{M_i}{M_j}\right)^{\frac{1}{4}}\right]^2 \qquad (2)$$

Further M_i is the molecular weight of the i th component and λ°_i is its value of thermal conductivity with internal degree frozen. Values of λ_{mix} obtained on the basis of (1) and (2) are referred to as approximate.

Semi-theoretical—In the above procedure some loss of accuracy is due to the various approximations made in deriving the explicit expression for φ_{ij}. This can be partly compensated if one value of λ_{mix} is known so that it is possible to dispense with the detailed form of relation (2) for φ_{ij}. Based on equation (2), Mathur & Saxena have shown that

$$\frac{\varphi_{ij}}{\varphi_{ji}} = \frac{\lambda^\circ_i}{\lambda^\circ_j} = \frac{\eta_i\, M_j}{\eta_j\, M_i} \tag{3}$$

η being the coefficient of viscosity. Thus the two constants φ_{12} and φ_{21} can be easily determined from (1) and (3) if one value of λ_{mix} is also known. This computation procedure, which is designated as semi-theoretical, is likely to yield good results as φ_{ij} values thus get adjusted through the use of one value of λ_{mix}. The only disadvantage is the requirement of a mixture conductivity value, but this is more than compensated by the enhancement in the accuracy, both in correlation of λ_{mix} data over the entire composition range and also for prediction at high temperatures.

Empirical—Further, if binary λ_{mix} values be known at two compositions then both the constants φ_{12} and φ_{21} of (1) can be directly determined by treating them as disposable parameters. Off hand this procedure should yield the maximum accuracy for reasons mentioned above. This *empirical method* introduced by Srivastava & Saxena[8] will also be studied.

Here a mention of the Hirschfelder's expression is made for λ_{mix} according to which

$$\lambda_{mix} = \lambda^\circ_{mix} + \sum_{j=1}^{n} \frac{\lambda_i - \lambda^\circ_i}{1 + \sum\limits_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{x_i} \cdot \frac{D_{ii}}{D_{ij}}} \tag{4}$$

Here λ°_{mix} is the conductivity of the mixture with frozen internal degrees of freedom, D_{ii} and D_{ij} are the values of the self and mutual diffusion coefficients respectively. The improved expression for λ_{mix} as given by Saxena *et al*[7] is as follows:

$$\begin{aligned}\lambda_{mix} = {} & \lambda^\circ_{mix} + \sum_{i=1} n\, [D_i]_{mix}\, [C'_i]_{mix} - \lambda^\circ_{mix} \sum_{i=1}^{v} \frac{[C_i]_{mix}}{[C_{vi}]_{mix}} \times \\ & \left\{1 - exp\left(-\frac{1}{[Z_i]_{mix}} \frac{[C_{vi}]_{mix}}{C_{vtr}}\right)\right\} + C_{vtr} \sum_{i=1}^{n} n\, [D_i]_{mix} \frac{[C'_i]_{mix}}{[C_{vi}]_{mix}} \times \\ & \left\{1 - exp\left(-\frac{1}{[Z_i]_{mix}} \frac{[C_{vi}]_{mix}}{C_{vtr}}\right)\right\}\end{aligned} \tag{5}$$

Here the various terms are as defined by them[7]. It is important to note here that the first two terms of (5) are same as (4) while the remaining two terms appear as correction when translational -internal energy exchange is considered. Relation of (5) is much more complicated than that of (4) but the contribution of correction terms is appreciable in many actual systems[7].

EXPERIMENTAL DATA

Recently Mathur & Saxena have considered the λ_{mix} data of a large number of binary and a few ternary systems. These systems are relatively simpler in the sense that most of the binary combinations included a rare gas and a simple diatomic gas *viz.*, hydrogen, oxygen or nitrogen. They also considered combinations with methane and carbon dioxide. It is proposed to study systems which are more complicated in as much as these involve polyatomic molecules containing many internal degrees of freedom. Obviously, even the application of rigorous theory[7] is not possible for such systems due to the lack of knowledge about the various fundamental constants like Z etc. For practical needs such systems are relatively more important and investigation is to be made for the prospect of utilising the methods mentioned under 'Methods' to predict and correlate the λ_{mix} values particularly where direct measured values are not available. The λ_{mix} data of the fourteen binary systems considered here have been plotted to check their relative consistency. In all cases except N_2—N_2O, NO—N_2O and O_2—N_2O, the data were found to be smooth and therefore the directly reported values have been used as such. Even for these three systems where the observed points differ from the smooth curve by a couple of per cent on the average and record have been made of the direct observed values. The experimental data of binary mixtures as well as of the related pure components are of Cheung, *et al*[9]. for O_2—CO_2 He—CO_2 (316°C), CH_4—C_3H_8, CO_2—C_3H_8, He—CH_4 and N_2—O_2; Weber[10] for H_2—CO_2 (0°C); Kornfeld & Hilferding[11] for H_2—CO_2 (25°C) and H_2—C_2H_4; Davidson & Music[12] for He—CO_2 (0°C); Ibbs & Hirst[13] for H_2—N_2O and H_2—CO; Keyes[14] for N_2—CO_2 (50°, 150°, 250° and 350°C); Rothman[15] for N_2—CO_2 (472°, 573°, 677° and 774°C); Westenberg & de Hass[16] for N_2—CO_2 (27°, 227° and 727°C) and Pereira & Raw[17] for N_2—N_2O, O_2—N_2O and NO—N_2O. Pure viscosity data were read from the smooth plots of viscosity versus temperature. All the available information was pooled for this purpose. The values employed in the calculations are recorded in Table 1 where the pure λ data are also indicated together with the temperature to which these refer. In Table 2 likewise are listed the λ_{mix} data as a function of composition at the appropriate temperature. For each system λ_{mix} values at lowest temperature are recorded in Table 2, while in Table 4 are listed the values for those systems only where λ_{mix} data also exist at higher temperatures.

TABLE 1

EXPERIMENTAL λ (CAL CM^{-1} SEC^{-1} DEG^{-1}) AND η (GM CM^{-1} SEC^{-1}) DATA USED IN COMPUTATION OF φ_{ij} AND λ_{mix}

Gas Pair	t °C	$\lambda_1 \times 10^5$	$\lambda_2 \times 10^5$	$\eta_1 \times 10^5$	$\eta_2 \times 10^5$
He—CH_4	316	20·29	55·6	18·95	31·50
He—CO_2	0	3·39	33·21	13·60	18·55
H_2—CO_2	0	3·393	41·63	13·60	8·40
H_2—CO	0	5·3	40·4	16·50	8·40
H_2—N_2O	0	3·8	40·4	13·58*	8·54*
H_2—C_2H_4	25	5·27	43·7	10·26	8·90
O_2—N_2	319	11·62	10·70	33·90	28·90
O_2—CO_2	97	5·218	7·66	18·15	24·30
O_2—N_2O	31·85	4·55	6·58	15·07	20·95
N_2—CO_2	50	4·34	6·64	15·95	18·05
N_2—N_2O	31·85	4·55	6·33	15·07	20·95
NO—N_2O	50·55	4·72	6·77	15·97	20·47
C_3H_8—CH_4	95	6·344	10·49	9·875	13·15
C_3H_8—CO_2	95	6·344	5·181	9·875	18·10

NOTE—Subscript 1 refers to the heavier component.

*Trautz, M. & Kurz, F. *Ann. Physik,* 9 (1931), 981.

TABLE 2

COMPARISON OF EXPERIMENTAL AND CALCULATED λ_{mix} (CAL CM^{-1} SEC^{-1} DEG^{-1}) VALUES. X_1 IS THE MOLE FRACTION OF THE HEAVIER COMPONENT

Gas pair and Temperature	X_1	Experimental	Approximate	% Deviation	Semi-theoretical	% Deviation	Empir	% Deviation
He—CH_4 (316°C)	0·254	40·63	38·32	—5·7	37·82	—6·9	..	..
	0·450	30·54	30·97	+1·1	..	..	30·36	—0·6
	0·701	24·53	24·93	+1·6	24·69	+0·7	..	..
He—CO_2 (0°C)	0·26	17·83	16·57	—7·1	17·80	—0·2	..	..
	0·48	11·20	10·29	—8·1	..	..	11·25	+0·4
	0·75	6·35	5·92	—6·8	6·32	0·5	..	..
H_2—CO_2 (0°C)	0·057	35·90	36·51	+1·7	36·3	+1·1	36·25	+1·0
	0·1654	28·00	28·69	+2·5	28·3	+1·1	..	..
	0·3932	17·24	17·61	+2·1	..	..	17·24	+0·0
	0·6302	10·34	10·26	—0·8	10·16	—1·7	10·18	—1·5
	0·8299	6·07	6·16	+1·5	6·06	—0·2	..	..
	0·906	4·77	4·85	+1·7	4·79	+0·4	4·80	+0·6
	0·9247	4·48	4·54	+1·3	4·50	+0·4	4·50	+0·4
H_2—CC (0°C)	0·206	27·0	27·5	+1·9	26·9	—0·4	27·9	+3·3
	0·366	20·9	20·5	—1·9	19·9	—4·8	..	..
	0·434	18·0	18·1	+0·6	..	..	18·1	+0·6
	0·728	10·3	10·2	—1·0	10·0	—3·0	..	..
	0·837	8·0	8·0	+0·0	7·9	—1·3	8·1	+1·3
H_2—N_2O (0°C)	0·188	27·2	26·7	—1·8	26·6	—2·2	26·8	—1·5
	0·401	17·0	17·1	+0·6	..	..	..	..
	0·614	10·7	10·9	+1·9	10·8	+0·9	10·8	+0·9
	0·791	7·1	7·1	+0·0	7·1	+0·0	..	..
H_2—C_2H_4 (25°C)	0·1351	32·9	32·3	—1·8	33·3	+1·2	33·4	+1·5
	0·389	20·6	19·4	—5·8	20·4	—1·0	..	..
	0·4863	16·90	16·04	—5·1	..	..	17·12	+1·3
	0·686	11·48	10·81	—5·8	11·33	—1·3	..	..
	0·8302	8·61	7·95	—7·7	8·23	—4·4	8·31	—3·5
O_2—N_2 (319°C)	0·6098	11·19	10·93	—2·3	11·24	+0·4	11·37	+1·6
O_2—CO_2 (97°C)	0·222	7·027	6·799	—3·2	7·013	—0·2	7·019	—0·1
	0.464	6·383	6·120	—4·1	..	..	..	..
	0·685	5·883	5·669	—3·8	5·868	—0·3	5·876	—0·1
	0·73	5·777	5·591	—3·2	5·770	—0·1	..	..
O_2—N_2O (31·85°C)	0·155	6·21	6·04	—2·7	6·25	+0·6	6·20	—0·2
	0·331	5·55	5·56	+0·2	5·87	+5·8	..	..
	0·544	5·43	5·13	+1·8	..	..	5·28	—2·8
	0·725	4·95	4·85	—2·0	5·07	+2·4	..	..
N_2—CO_2 (50°C)	0·335	5·67	5·55	—2·1	5·69	+0·4	..	..
	0·4712	5·37	5·22	—2·8	..	..	5·41	+0·7
	0·6594	4·99	4·84	—3·0	4·96	—0·6	..	..
N_2—N_2O (31·85°C)	0·142	5·77	5·90	+2·3	5·71	—1·0	5·89	+2·0
	0·408	5·26	5·30	+0·8	4·97	—5·5	..	..
	0·562	4·75	5·04	+6·1	..	..	4·98	+4·8
	0·758	4·73	4·78	+1·1	4·59	—3·0	..	..
	0·766	4·69	4·78	+1·9	4·59	—2·1	4·72	+0·6
NO—N_2O (50·55°C)	0·271	5·41	5·91	+9·3	6·16	+13·9	6·23	+15·1
	0·455	5·77	5·49	—4·9	..	..	..	..
	0·672	5·28	5·11	—3·2	5·33	+0·9	5·40	+2·3
	0·767	5·20	4·98	—4·2	5·15	—1·0	..	..
C_3H_8—CH_4 (95°C)	0·221	8·841	8·85	+0·4	8·964	+1·4	..	..
	0·514	7·636	7·564	—0·9	..	..	7·635	—0·0
	0·687	7·083	7·035	—0·7	7·096	+0·2	..	..
C_3H_8—CO_2 (95°C)	0·365	5·715	5·447	—4·7	5·666	—0·9	..	..
	0·551	5·884	5·675	—3·6	..	..	5·911	+0·5
	0·709	6·083	5·896	—3·1	6·056	—0·4	..	..

CALCULATION OF THERMAL CONDUCTIVITY

The procedures of calculating thermal conductivity have already been outlined under 'Methods'. The results obtained on the different systems are reported here. The values of λ_{mix} , according to (1) and (2) are listed in column 4 of Table 2. The experimental values of λ_{mix} and the percentage deviation between the experimental and calculated values are also recorded in columns 3 and 5 of Table 2 respectively. The factor $(\lambda^\circ_i / \lambda^\circ_j)$ of (2) was computed from (3) using the viscosity data. The semi-theoretical calculated values are reported in column 6 of Table 2 and are based on (1) and (3). The λ_{mix} value invariably around the middle composition was employed in this calculation. The percentage deviation of the semi-theoretical values from the experimental values are reported in column 7 of this very Table. Lastly, the computed λ_{mix} values, according to the empirical method, are given in column 8 and their percentage deviation from the experimental values in column 9. A remark regarding this method of calculation is relevant. As the equations giving φ_{12} and φ_{21} become quadratic, we get two sets of coupled φ_{ij} values but on the basis of the reproduction of λ_{mix} values, it is always possible to select one set which gives better agreement with experiment. The φ_{ij} values obtained according to the approximate, empirical and semi-theoretical procedures are recorded in Table 3.

There are reasons to believe that φ_{ij} values are very weakly dependent upon temperature and composition. We employ this fact to compute λ_{mix} at higher temperatures. Out of the fourteen gas pairs given in Table 3, there are six pairs for which experimental λ_{mix} values are also available at higher temperatures. These systems are reported only in Table 4 and experimental as well as calculated values according to all the three procedures are reported along with the percentage deviations in all cases.

For a few systems the λ_{mix} values are also computed on the basis of the expression of Hirschfelder, equation (4), and these are recorded in Table 5. These calculations are, according to the Lennard-Jones (12–6), potential using parameters as given by Hirschfelder Curtiss & Bird[18] (first set). The expression for λ°_{mix} employed is that of Muckenfuss & Curtiss[19] as modified by Mason & Saxena[20].

Lastly, in Table 6 the thermal conductivity values for the ternary system N_2—O_2—CO_2 are reported. The φ_{ij} needed in this calculation were computed at 97°C for O_2—CO_2,

TABLE 3

VARIOUS COMPUTED φ_{ij} VALUES

Gas Pair	t °C	Approximate		Empirical		Semi-theoretical	
		Φ_{12}	Φ_{21}	Φ_{22}	Φ_{21}	Φ_{12}	Φ_{21}
He—CH_4	316	0·4035	2·687	0·1035	4·280	0·4141	2·759
He—CO_2	0	0·2352	3·657	0·3246	3·031	0·2125	3·178
H_2—CO_2	0	0·1988	2·736	0·2868	2·770	0·2102	2·834
H_2—CO	0	0·7259	2·121	0·1556	2·479	0·3504	2·478
H_2—N_2O	0	0·1975	2·768	0·1110	2·868	0·2032	2·790
H_2—C_2H_4	25	0·2360	2·849	0·2918	2·471	0·2158	2·605
O_2—N_2	319	1·0790	1·050	0·6805	1·449	1·0170	0·9907
O_2—CO_2	97	0·7898	1·454	0·7695	1·282	0·7273	1·339
O_2—N_2O	31·85	0·7764	1·486	0·3480	2·302	0·6924	1·324
N_2—CO_2	50	0·7803	1·445	0·5880	1·549	0·7376	1·366
N_2—N_2O	31·85	0·7737	1·460	1·072	1·192	0·8711	1·639
NO—N_2O	50·55	0·7790	1·465	0·7295	1·235	0·7056	1·327
C_3H_8—CH_4	95	0·5443	1·993	0·3874	2·370	0·5318	1·947
C_3H_8—CO_2	95	0·8041	1·477	0·7432	1·316	0·7442	1·367

TABLE 4

COMPARISON OF EXPERIMENTAL AND CALCULATED λ_{mix} VALUES USING ϕ_{ij} VALUES OF A LOWER TEMPERATURE

Gas Pair and Temp.	X_1	Exptl.	Approx.	%Dev.	Semi-theoret.	%Dev.	Empir.	%Dev.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
He—CO_2 (316°C)	0·00	55·6	..	..	..	..	..	..
	0·39	23·65	23·66	+0·0	25·53	+7·9	25·27	+6·8
	1·00	9·58	..	..	..	..	..	..
H_2—CO_2 (25°C)	0·00	43·7	..	..	..	..	..	..
	0·0362	40·2	40·3	+0·2	40·1	—0·2	40·1	—0·2
	0·0941	35·0	35·4	+1·1	35·1	+0·3	35·0	+0·0
	0·504	15·13	14·97	—1·1	14·64	—3·2	14·64	—3·2
	0·807	7·58	7·41	—2·2	7·29	—5·2	7·29	—5·2
	0·953	4·43	4·81	+8·6	4·68	+5·6	4·79	+8·1
	1·00	4·08	..	..	..	..	..	..
O_2—N_2O (50·55°C)	0·00	6·58	..	..	..	..	..	..
	0·169	6·51	6·19	—4·9	6·41	—1·5	6·36	—2·3
	0·35	6·13	5·70	—7·0	6·02	—1·8	5·89	—3·9
	0·481	6·30	5·42	—13·9	5·75	—8·7	5·60	—11·1
	0·623	5·83	5·17	—11·1	5·45	—6·5	5·31	—8·9
	0·775	5·00	4·96	—0·8	5·15	+3·0	5·05	+1·0
	0·874	4·99	4·84	—3·0	4·96	—0·6	4·89	—2·0
	1·00	4·72	..	..	..	..	..	..
O_2—N_2O (101°C)	0·00	7·69	..	..	..	..	..	..
	0·231	7·01	6·93	—1·1	7·25	+3·4	7·22	+3·0
	0·241	6·99	6·90	—1·3	7·21	+3·1	7·20	+3·0
	0·382	6·75	6·57	—2·7	6·96	+3·1	6·87	+1·8
	0·549	6·41	6·27	—2·2	6·63	+3·4	6·52	+1·7
	0·699	6·01	6·06	+0·8	6·34	+5·5	6·24	+3·8
	0·723	5·94	6·03	+1·5	6·29	+7·1	6·20	+4·4
	1·00	5·78	..	..	..	..	..	..
O_2—N_2O (140·2°C)	0·00	8·33	..	..	..	..	..	..
	0·232	7·51	7·52	+0·1	7·87	+4·8	7·85	+4·5
	0·306	7·39	7·32	—0·9	7·72	+4·5	7·60	+2·8
	0·495	6·99	6·92	—1·0	7·33	+4·9	7·22	+3·6
	0·796	6·38	6·50	+1·9	6·72	+5·3	6·64	+4·1
	1·00	6·32	..	..	..	..	..	..
O_2—N_2O (180·1°C)	0·00	9·09	..	..	..	..	..	..
	0·286	8·10	8·11	+0·1	8·53	+5·3	8·52	+5·2
	0·40	8·03	7·84	—2·4	8·30	+3·4	8·24	+2·6
	0·635	7·14	7·43	+4·1	7·82	+9·5	7·54	+6·2
	0·727	7·10	7·32	+3·1	7·63	+7·5	7·72	+8·1
	1·00	7·08	..	..	..	..	..	..
N_2—CO_2 (150°C)	0·00	8·31	..	..	..	..	..	..
	0·335	7·64	7·27	—4·8	7·47	—2·2	7·56	—1·1
	0·4712	7·38	6·98	—5·4	7·18	—2·7	7·27	—1·5
	0·6594	7·02	6·66	—5·1	6·82	—2·8	6·89	—1·9
	1·00	6·27	..	..	..	..	..	..
N_2—CO_2 (250°C)	0·00	9·83	..	..	..	..	..	..
	0·335	9·36	8·97	—4·2	9·22	—1·5	9·38	+0·2
	0·4712	9·21	8·75	—5·0	9·01	—2·2	9·17	—0·4
	0·6594	8·91	8·55	—4·0	8·75	—1·8	8·87	—0·4
	1·00	8·36	..	..	..	..	..	..
N_2—CO_2 (350°C)	0·00	11·22	..	..	..	..	..	..
	0·335	11·30	10·64	—5·8	10·94	—3·2	11·17	—1·2
	0·4712	11·27	10·55	—6·4	10·85	—3·7	11·08	—1·7
	0·6594	11·04	10·50	—4·9	10·74	—2·7	10·92	—1·1
	1·00	10·58	..	..	..	..	..	..
N_2—CO_2 (472°C)	0·00	12·32	..	..	..	..	..	..
	0·44	12·56	11·87	—5·5	12·21	+2·8	12·50	—0·5
	1·00	12·15	..	..	..	..	..	..

contd.

TABLE 4—*contd.*

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
N_2—CO_2 (573°C)	0·00	13·39	..	..	..	..	..	..
	0·33	14·19	13·19	—7·0	13·56	—4·4	13·92	—1·9
	0·50	14·17	13·27	—6·4	13·64	—3·7	13·99	—1·3
	0·67	14·03	13·42	—4·3	13·72	—2·2	14·14	+0·8
	1·00	13·87	..	..	..	..	..	..
N_2—CO_2 (677°C)	0·00	15·12	..	..	..	..	..	..
	0·50	16·27	15·23	—6·4	15·66	—3·7	16·07	—1·2
	1·00	61·10	..	..	..	..	..	..
N_2—CO_2 (774°C)	0·00	16·99	..	..	..	..	..	..
	0·50	18·28	17·22	—5·8	17·71	—3·1	18·19	—0·5
	1·00	18·29	..	..	..	..	..	..
N_2—CO_2 (300°K)	0·00	6·13	..	..	..	..	..	..
	0·25	5·25	5·31	+1·1	5·44	+3·6	5·27	+0·4
	0·50	4·90	4·72	—1·6	4·85	—1·0	4·54	—7·3
	0·75	4·30	4·27	—0·7	4·36	+1·4	3·92	—8·8
	1·00	3·93	..	..	..	..	..	..
N_2—CO_2 (500°K)	0·00	9·16	..	..	..	..	..	..
	0·25	8·90	8·52	—4·3	8·72	—2·0	8·86	—0·4
	0·50	8·75	8·13	—7·1	8·36	—4·5	8·51	—2·7
	0·75	8·20	7·91	—3·5	8·06	—1·7	8·14	—0·7
	1·00	7·80	..	..	..	..	..	..
N_2—CO_2 (1000°K)	0·00	15·7	..	..	..	..	..	..
	0·25	16·4	15·6	—4·9	16·0	—2·5	16·4	+0·0
	0·50	17·1	15·9	—7·0	16·3	—4·7	16·7	—2·3
	0·75	16·3	16·3	—0·0	16·6	+1·8	16·8	+3·1
	1·00	16·8	..	..	..	..	..	..
N_2—N_2O (50·55°C)	0·00	6·58	..	..	..	..	..	..
	0·253	5·44	5·84	+7·4	5·55	+2·0	5·82	+7·0
	0·601	4·97	5·17	+4·0	4·89	—1·8	5·11	+2·8
	0·746	4·96	4·98	+0·4	4·77	—3·8	4·92	—0·8
	0·825	4·94	4·89	—1·0	4·74	—4·0	4·84	—2·0
	1·00	4·72	..	..	..	..	..	..
N_2—N_2O (101°C)	0·00	7·35	..	..	..	..	..	..
	0·201	6·72	6·79	+1·0	6·50	—3·3	6·75	+0·4
	0·441	6·46	6·33	—2·0	5·95	—7·9	6·24	—3·5
	0·501	6·29	6·25	—0·6	5·87	—6·7	6·14	—2·4
	0·699	6·29	6·01	—4·5	5·73	—8·9	5·91	—6·0
	0·776	·616	5·94	—3·6	5·72	—7·1	5·85	—5·0
	1·00	5·78	..	..	..	..	..	..
N_2—N_2O (140·2°C)	0·00	7·80	..	..	..	..	..	..
	0·197	7·30	7·27	—0·4	6·95	—4·8	7·21	—1·2
	0·385	6·47	6·90	+6·6	6·49	+3·1	6·80	+5·1
	0·561	6·58	6·66	+1·2	6·28	—4·6	6·53	—0·8
	0·70	6·40	6·52	+1·9	6·22	—2·8	6·39	—0·2
	1·00	6·32	..	..	..	..	..	..
N_2—N_2O (180·1°C)	0·00	8·57	..	..	..	..	..	..
	0·248	8·23	7·90	—4·0	7·51	—8·7	7·82	—5·0
	0·398	7·50	7·60	+0·1	7·17	—4·4	7·49	—0·1
	0·525	7·58	7·44	—1·8	7·01	—7·5	7·29	—3·8
	0·642	7·29	7·31	+0·3	6·94	—4·1	7·16	—1·8
	0·765	7·18	7·21	+0·4	6·94	—3·3	7·08	—1·4
	1·00	7·08	..	..	..	..	..	..

contd.

TABLE 4—*contd.*

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
NO—N_2O (101°C)	0·00	7·62	..	..	..	..	..	..
	0·174	7·25	7·05	—2·8	7·28	+0·4	7·34	+1·2
	0·298	6·98	6·74	—3·4	7·05	+1·0	7·13	+2·1
	0·548	6·79	6·26	—7·9	6·57	—3·2	6·66	—1·9
	0·736	6·26	6·02	—3·8	6·23	—0·5	6·30	+0·6
	1·00	5·78	..	..	..	..	..	..
NO—N_2O (140·2°C)	0·00	8·11	..	..	..	..	..	..
	0·234	7·21	7·38	+2·4	7·68	+6·5	7·75	+7·5
	0·498	6·89	6·85	—0·6	7·19	+4·4	7·29	+5·8
	0·760	6·58	6·51	—1·1	6·73	+2·3	6·79	+3·2
	0·767	6·34	6·50	+2·5	6·72	+6·0	6·77	+6·8
	1·00	6·32	..	..	..	..	..	..
NO—N_2O (180·1°C)	0·00	9·01	..	..	..	..	..	..
	0·172	8·43	8·40	—0·4	8·67	+2·8	8·74	+3·7
	0·230	8·19	8·23	+0·5	8·56	+4·5	8·64	+5·5
	0·239	8·11	8·21	+1·2	8·54	+5·3	8·58	+5·8
	0·717	7·46	7·34	—1·6	7·60	+1·9	7·68	+3·1
	1·00	7·08	..	..	..	..	..	..

50°C for N_2—CO_2 and 319°C for N_2—O_2 in all the three methods. This procedure also seeks justification in the fact that φ_{ij} may be regarded as temperature and composition independent.

DISCUSSION

An idea of the relative success of the approximate, semi-theoretical and empirical procedures for computing λ_{mix} can be formed by looking at the percentage deviations in Table 2. It is found that all the methods can reproduce the experimental values on the average within a few per cent, though the deviations in certain cases exceed the uncertainties of the experimental data. To have a more precise idea we calculate the average absolute

TABLE 5

COMPARISON OF EXPERIMENTAL AND RIGOROUSLY CALCULATED λ_{mix} VALUES

Gas Pair	Temp. °C	Mole-fraction X_1	$\lambda_{exptl.}$	$\lambda_{calcd.}$	% Dev.
He—CH_4	316	0·254	40·63	38·70	—4·8
		0·450	30·54	31·06	+1·7
		0·701	24·53	24·87	+1·4
He—CO_2	0	0·26	17·83	17·44	—2·2
		0·48	11·20	10·78	—3·8
		0·75	6·35	6·10	—3·9
He—CO_2	316	0·39	23·65	24·50	+3·6
O_2—CO_2	97	0·222	7·027	7·319	+4·2
		0·464	6·383	6·465	+1·3
		0·685	5·883	5·867	—0·3
		0·730	5·777	5·761	—0·3

TABLE 6

COMPARISON OF EXPERIMENTAL AND CALCULATED λ_{mix} VALUES FOR THE TERNARY MIXTURE N_2—O_2—CO_2 AT 97°C. THE CONCENTRATIONS ARE $X_{N_2}=0\cdot3231$, $X_{O_2}=0\cdot3729$ AND $X_{CO_2}=0\cdot3040$

λ exptl.	λ calcd. approx.	% dev.	λ calcd. semi-theoret.	%dev.	λ calcd. empirical	% dev.
6·729	6·372	—5·3	6·665	—1·0	6·714	—0·2

deviation for each system and these are indicated in Table 7. The experimental data for the systems O_2—N_2O, N_2—N_2O and NO—N_2O are not smooth, the scatter is several per cent and therefore we have not given proportionate weight to the deviations encountered in these cases. We then find that pronounced disagreement is found only for He—CO_2 and H_2—C_2H_4 for the aprroximate method. The semi-theoretical as well as empirical procedures always lead to satisfactory results. The average absolute deviations for all the systems of Table 2 are, 3·0% for the approximate method, 1·7% for the semi-theoretical method, and 1·6% for the empirical method. Thus we find that, although all the methods are reasonably successful, the semi-theoretical and empirical procedures are somewhat preferable. This result is based on the computations of Table 2 only.

TABLE 7

AVERAGE ABSOLUTE PERCENTAGE DEVIATION SYSTEMWISE FOR COMPUTED AND EXPERIMENTAL VALUES OF TABLE 2

Gas Pair and Temperature	Approximate	Semi-theoretical	Empirical
He-CH_4 (316°C)	2·8	3·8	0·6
He—CO_2 (0°C)	7·3	0·4	0·4
H_2—CO_2 (0°C)	1·7	0·8	0·7
H_2—CO (0°C)	1·1	2·4	1·7
H_2—N_2O (0°C)	1·1	1·0	1·2
H_2—C_2H_4 (25°C)	5·2	2·0	2·1
O_2—N_2 (319°C)	2·3	0·4	1·6
O_2—CO_2 (97°C)	3·6	0·2	0·1
O_2—N_2O (31·85°C)	1·7	2·9	1·5
N_2—CO_2 (50°C)	2·6	0·5	0·7
N_2—N_2O (31·85°C)	2·4	2·9	2·5
NO—N_2O (50·55°C)	5·4	5·3	8·7
C_3H_8—CH_4 (95°C)	0·7	0·8	0·0
C_3H_8—CO_2 (95°C)	3.8	0·7	0·5

Records of Table 4, in general, support the validity of λ_{mix} calculations based on the assumption of temperature independent ϕ_{ij}. The deviations no doubt assume in many cases somewhat enhanced magnitudes. To facilitate such a study of the average absolute percentage deviations systemwise a report has been given in Table 8. The deviations in Table 4, in many cases, can be justified on the basis of the experimental data being uncertain also. More illuminating are the figures of the percentage average absolute deviations for all the systems of Table 4. It is found that these numbers are 3·3, 3·8 and 2·9 for the approximate

TABLE 8

AVERAGE ABSOLUTE PERCENTAGE DEVIATION SYSTEMWISE FOR COMPUTED AND EXPERIMENTAL VALUES OF TABLE 4

Gas Pair and Temperature	Approximate	Semi-theoretical	Empirical
He—CO_2 (316°C)	0·0	7·9	6·8
H_2—CO_2 (25°C)	2·6	2·9	3·3
O_2—N_2O (50·55°C)	6·8	3·7	4·9
O_2—N_2O (101°C)	1·6	4·3	3·0
O_2—N_2O (140·2°C)	1·0	4·9	3·8
O_2—N_2O (180·1°C)	2·4	6·4	5·5
N_2—CO_2 (150°C)	5·1	2·6	1·5
N_2—CO_2 (250°C)	4·4	1·8	0·3
N_2—CO_2 (250°C)	5·7	3·2	1·3
N_2—CO_2 (472°C)	5·5	2·8	0·5
N_2—CO_2 (573°C)	5·9	3·4	1·3
N_2—CO_2 (677°C)	5·8	3·1	0·5
N_2—CO_2 (300°K)	1·1	2·0	5·0
N_2—CO_2 (500°K)	5·0	2·7	1·3
N_2—CO_2 (1000°K)	4·0	3·0	1·8
N_2—N_2O (50·55°C)	3·2	2·9	3·2
N_2—N_2O (101°C)	2·3	6·8	3·5
N_2—N_2O (140·2°C)	2·5	3·8	1·8
N_2—N_2O (180·1°C)	1·3	5·6	2·4
NO—N_2O (101°C)	4·5	1·3	1·5
NO—N_2O (140·2°C)	1·7	4·8	5·8
NO—N_2O (180·1°C)	0·9	3·6	4·5

semi-theoretical and empirical procedures of computations. Thus for calculations of λ_{mix} at high temperatures all the methods are found almost equally good. However, the success of the approximate method at high temperatures is expected because of the better validity of some of the assumptions involved. The empirical and semi-theoretical procedures, on account of the way adopted for fixing ϕ_{ij} , get relatively more dependable. Further confirmation of these conclusions is obtained from the work of Mathur & Saxena.

The rigorous calculated values for the three systems listed in Table 5 are also in agreement with the experimental values usually in the same order of magnitude as the above methods. The average absolute deviations for all the eleven mixtures of Table 5 is $2{\cdot}5\%$. This puts more importance to the above computations which besides being easy require much less initial input information.

The ternary system calculations given in Table 6 are of very interesting curiosity besides being very useful. It is found that the approximate method is rather poor in reproducing λ_{mix} though semi-theoretical and empirical procedures are excellent.

It is interesting to examine the validity of a relation of the type of (1) for predicting and correlating λ_{mix} data for polyatomic molecules. For such systems the relation of (5) must be the starting working formula. This has also been investigated by Saksena & Saxena. Their work reveals that for polyatomic molecules, (5) reduces to (1) only with a new definition for λ_i . We now get in its place λ_{eff} defined as follows :

$$\lambda_{eff} = \lambda'_i \left[1 + \frac{1}{[\,Z_i\,]_{mix}}\right] - \lambda^{\circ}_i \left[\frac{1}{[\,Z_i\,]_{mix}} \left\{1 + \frac{[\,C'_i\,]_{mix}}{C_{vtr}}\right\}\right] \qquad (6)$$

Here the various terms are as defined by Saksena & Saxena. In all complicated polyatomic molecules λ_{eff} is appreciably different from λ_i and the Wassiljewa form (1) is inadequate to interpret λ_{mix} data. This explains, to a large extent, the poor agreement found for many complicated systems in Tables 3 and 4. For such cases, because of the flexibility and appropriateness of form, (1) may still continue to be precise enough for correlation specially for semi-theoretical and empirical procedures.

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