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Calculation of thermal conductivities of two binary gas mixtures

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Abstract: The alternative procedures are proposed for the calculation of thermal conductivities of binary gas mixtures and applied to N_2-N_2O and O_2-N_2O at five temperatures. The theoretical values are compared with the experimental values.

1. Introduction

Lindsay and Bromley (1950) proposed the method for the calculation of Wassiljewa coefficients of Wassiljewa equation (Wassiljewa 1904) for the thermal conductivities of binary gas mixtures. Mason and Saxena (1958) also proposed another method to estimate Wassiljewa coefficients for the same purpose. In both these methods, the viscosities of pure gas components are required. Without their knowledge the calculation of Wassiljewa coefficients is not possible.

In the present paper the alternative procedures have been suggested to estimate Wassiljewa coefficients for thermal conductivities of binary gas mixtures and applied to N_2-N_2O and O_2-N_2O using Hirschfelder Eucken approximation and Lindsay-Bromley or Mason-Saxena method. The theoretical values are compared with the experimental values (Pereira and Raw 1963). The modified expressions of Lindsay-Bromley and Mason-Saxena methods eliminate the viscosity terms of gas components.

2. Theory

Wassiljewa equation (Wassiljewa 1904) have been successfully utilized for the thermal conductivities of binary gas mixtures and it may be written as,

$$\lambda = \frac{\lambda_i}{1+A_{ij}.x_j\,|\,x_i} + \frac{\lambda_j}{1+A_{ji}\,x_i\,|\,x_j} \tag{1}$$

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where λ and λ_i are the thermal conductivities of the mixture and the pure gas component i; x_i is the mole fraction of component i and A_{ij} is one two sets of Wassiljewa coefficients. Cowling *et al* (1963). Cowling (1961) and Wright and Gray (1962) have suggested the importance of A_{ij}.

Two different theoretical approximations for Wassiljewa coefficient A_{ij} of Wassiljewa equation have already been suggested. One of them is a semi-empirical equation due to Lindsay and Bromley (1950),

$$A_{ij} = \frac{1}{4}\left[1+\left\{\frac{\eta_i}{\eta_j}\left(\frac{M_j}{M_i}\right)^{3/4}\frac{T+S_i}{T+S_j}\right\}^{\frac{1}{2}}\right]^2\frac{T+S_{ij}}{T+S_i} \tag{2}$$

where η_i, η_j and M_i, M_j are respectively the viscosities and molecular weights of components i, j, S is Sutherland's constant and $S_{ij} = (S_i, S_j)^{\frac{1}{2}}$ when the both gases are nonpolar, as considered here.

Another approximation for Wassiljewa coefficients obtained from rigorous theory has been derived by Mason and Saxena (1958),

$$A_{ij} = 0{\cdot}3765\left(1+\frac{M_i}{M_j}\right)^{-\frac{1}{2}}\left[1+\left(\frac{\eta_i}{\eta_j}\right)^{\frac{1}{2}}\left(\frac{M_j}{M_i}\right)^{1/4}\right]^2 \tag{3}$$

Hirschfelder and Eucken (1964) have given the first approximation to the thermal conductivity of pure polyatomic gas taking into approximately the transfer of energy between translational and internal degrees of freedom in molecules. The approximation relates the thermal conductivity to the viscosity in the following way,

$$[\lambda]_1 = \frac{15R}{4M}\left(\frac{4C_v}{15R}+\frac{3}{5}\right)[\eta]_1 \tag{4}$$

where R and C_v are molar gas constant and molar heat capacity at constant volume respectively

For better values, the higher third approximation (Hirschfelder *et al* 1964) to the coefficient of thermal conductivity have been taken and is represented as follows,

$$[\lambda]_1 = [\lambda]_1 f^3{}_\lambda = \frac{15R}{4M}\left(\frac{4C_v}{15R}+\frac{3}{5}\right)[\eta]_1 f^3{}_\lambda. \tag{5}$$

The approximation factors $f^3{}_{\lambda i}$ and $f^3{}_{\lambda j}$ are very close to unity (Hirschfelder *et al* 1964). Hence the approximation $f^3{}_{\lambda i}/f^3{}_{\lambda j} \approx 1$ may be adopted.

It may be noticed (Hirschfelder *et al* 1964) that the order of $[\lambda_i]_1/[\lambda_j]_1$, $[\lambda_i]_3/[\lambda_j]_3$ and λ_i/λ_j is the same and the order of $[\eta_i]_1/[\eta_j]_1$ and η_i/η_j is also the same. Therefore the following arbitrary approximations may be taken as,

$$\frac{[\lambda_i]_1}{[\lambda_j]_1} \approx \frac{[\lambda_i]_3}{[\lambda_j]_3} \approx \frac{\lambda_i}{\lambda_j} \text{ and } \frac{[\eta_i]_1}{[\eta_j]_1} \approx \frac{\eta_i}{\eta_j}. \tag{6}$$

With the help of equations (5) and (6), equations (2) and (3) can be transformed as,

$$A_{ij} = \frac{1}{4}\left[1+\left\{\frac{\lambda_i}{\lambda_j}\cdot\left(\frac{M_i}{M_j}\right)^{1/4}\cdot\frac{\frac{4}{15}C_{vj}+\frac{3}{5}R}{\frac{4}{15}C_{vi}+\frac{3}{5}R}\cdot\frac{T+S_i}{T+S_j}\right\}^{1/2}\right]^2\frac{T+S_{ij}}{T+S_i} \tag{7}$$

and

$$A_{ij} = 0\cdot3765\left(1+\frac{M_i}{M_j}\right)^{-1/2}\left[1+\left(\frac{\lambda_i}{\lambda_j}\right)^{1/2}\left(\frac{M_i}{M_j}\right)^{1/4}\left\{\frac{\frac{4}{15}C_{vj}+\frac{3}{5}R}{\frac{4}{15}C_{vi}+\frac{3}{5}R}\right\}^{1/2}\right]^2 \tag{8}$$

Equations (7) and (8) are separately used for the calculation of Wassiljewa coefficients and hence for the prediction of thermal conductivities The relation for molar heat capacity at constant pressure, C_p,

$$C_p = \alpha+\beta T+\gamma T^2+\delta T^3 \tag{9}$$

where α, β, γ and δ are constants (Glasstone 1974) dependent upon the nature of the gas, enables us to calculate the C_p, C_v of N_2. O_2, N_2O can be calculated from the knowledge of C_p from equation (9) and the difference of C_p and C_v (Chapman and Cowling 1970). The observed values of thermal conductivities of gas components at different temperatures are taken (Pereira and Raw 1963) and the Sutherland's constants used in equation (7) from the literature (Chapman and Cowling 1970).

3. Results and Discussion

The experimental (Pereira and Raw 1963) and the theoretical values of thermal conductivities N_2–N_2O and O_2–N_2O at various compositions and temperatures are represented in Tables 1 and 2 respectively and Wassiljewa coefficients in Table 3.

Table 1. Thermal conductivity (Cal km^{-1} sec^{-1} deg^{-1}) of nitrogen-nitrous oxide mixtures as a function of temperature.

Temperature °C	Mole fraction x_i	Exptl* λ	From equations (1) and (2) λ	From equations (1) and (7) λ	From equations (1) and (3) λ	From equations (1) and (8) λ
31.85	0.234	4.69	4.93	4.95	4.78	4.78
	0.242	4.73	4.94	4.97	4.78	4.79
	0.438	4.75	5.28	5.31	5.04	5.06
	0.592	5.26	5.55	5.59	5.30	5.32
	0.858	5.77	6.05	6.07	5.90	5.91
	Mean absolute	deviation	(6.22)	(6.77)	(2.42)	(2.66)
50.55	0.175	4.94	5.01	5.02	4.89	4.90
	0.254	4.96	5.15	5.16	4.99	4.99
	0.399	4.97	5.41	5.42	5.19	5.19
	0.747	5.44	6.07	6.08	5.85	5.86
	Mean absolute	deviation	(6.42)	(6.61)	(3.39)	(3.39)
101.0	0.224	6.16	6.11	6.12	5.95	5.95
	0.301	6.29	6.22	6.24	6.02	6.03
	0.499	6.20	6.53	6.55	6.26	6.28
	0.559	6.46	6.62	6.64	6.35	6.37
	0.799	6.72	7.01	7.03	6.81	6.82
	Mean absolute	deviation	(2.54)	(2.59)	(2.24)	(2.12)
140.2	0.300	6.40	6.75	6.77	6.53	6.55
	0.439	6.58	6.96	6.98	6.68	6.70
	0.615	6.47	7.22	7.24	6.93	6.95
	0.803	7.30	7.50	7.52	7.29	7.30
	Mean absolute	deviation	(6.40)	(6.69)	(2.70)	(2.90)
180.1	0.235	7.18	7.41	7.43	7.23	7.23
	0.358	7.29	7.58	7.61	7.34	7.36
	0.475	7.58	7.76	7.79	7.47	7.49
	0.602	7.50	7.95	7.98	7.65	7.67
	0.752	8.23	8.18	8.20	7.93	7.95
	Mean absolute	deviation	(3.23)	(3.48)	(1.70)	(1.68)

* experimental values are taken (Pereira and Raw 1963)

Table 2. Thermal conductivity (cal km^{-1} sec^{-1} deg^{-1}) of oxygen-nitrous oxide mixtures as a function of temperature.

Temperature °C	Mole fraction x_i	Exptl* λ	From equations (1) and (2) λ	From equations (1) and (7) λ	From equations (1) and (3) λ	From equations (1) and (8) λ
31.85	0.275	4.95	5.02	5.04	4.86	4.87
	0.456	5.43	5.36	5.38	5.13	5.15
	0.669	5.55	5.80	5.82	5.57	5.58
	0.845	6.21	6.20	6.21	6.04	6.05
	Mean absolute	deviation	(1.84)	(1.90)	(2.61)	(2.48)
50.55	0.126	4.99	4.93	4.94	4.84	4.85
	0.225	5.00	5.16	5.12	4.96	4.97
	0.377	5.83	5.39	5.41	5.17	5.19
	0.519	6.30	5.67	5.69	5.42	5.44
	0.650	6.13	5.95	5.97	5.70	5.72
	0.831	6.51	6.36	6.38	6.19	6.20
	Mean absolute	deviation	(4.80)	(4.15)	(6.84)	(6.58)
101.0	0.277	5.94	6.24	6.25	6.04	6.06
	0.301	6.01	6.28	6.30	6.07	6.09
	0.451	6.41	6.55	6.57	6.29	6.31
	0.618	6.75	6.87	6.89	6.59	6.62
	0.759	6.99	7.16	7.18	6.92	6.95
	0.769	7.01	7.18	7.20	6.96	6.98
	Mean absolute	deviation	(3.06)	(3.34)	(1.46)	(1.31)
140.2	0.204	6.38	6.67	6.68	6.50	6.52
	0.505	6.99	7.24	7.26	6.93	6.97
	0.694	7.39	7.63	7.65	7.34	7.38
	0.768	7.51	7.79	7.81	7.54	7.57
	Mean absolute	deviation	(3.78)	(4.02)	(0.96)	(0.85)
180.1	0.273	7.10	7.57	7.57	7.35	7.35
	0.365	7.14	7.74	7.75	7.47	7.47
	0.600	8.03	8.21	8.22	7.89	7.89
	0.714	8.10	8.45	8.46	8.16	8.16
	Mean absolute	deviation	(5.39)	(5.49)	(2.65)	(2.65)

* experimental values are taken (Pereira and Raw 1963)

Table 3. Wassiljewa coefficients for the mixtures of N_2-N_2O and O_2-N_2O

mixtures	Temperature °C	From eq. (2) :		From eq. (7)		From eq. (3) :		From eq. (8)	
		A_{ij}*	A_{ji}*	A_{ij}	A_{ji}	A_{ij}*	A_{ji}*	A_{ij}	A_{ji}
N_2–N_2O	31.85	1.26	0.76	1.23	0.76	1.45	0.78	1.41	0.80
	50.55	1.26	0.76	1.24	0.77	1.44	0.78	1.42	0.79
	101.0	1.24	0.78	1.20	0.80	1.42	0.79	1.37	0.82
	140.2	1.23	0.78	1.19	0.80	1.40	0.80	1.36	0.82
	180.1	1.22	0.80	1.19	0.81	1.40	0.80	1.36	0.82
O_2–N_2O	31.85	1.32	0.74	1.28	0.76	1.49	0.77	1.45	0.79
	50.55	1.31	0.75	1.28	0.76	1.48	0.78	1.45	0.79
	101.0	1.29	0.76	1.25	0.78	1.45	0.79	1.40	0.81
	140.2	1.28	0.77	1.25	0.78	1.44	0.80	1.40	0.81
	180.1	1.27	0.77	1.24	0.79	1.42	0.80	1.39	0.82

*A_{ij} values are taken from the reference (Pereira and Raw 1963)

Equation (7) like Lindsay-Bromley method overestimates the system N_2–N_2O generally at all five temperatures by about 2·5 to 6·8% and the system O_2–N_2O by about 1·9 to 5·5%. Though for each system equation (7) shows more absolute deviations than the corresponding Lindsay-Bromley method, the comparison is still satisfactory. Equation (8) like Mason-Saxena method overestimates the system N_2–N_2O by about 1·6 to 3·0% at four temperatures but underestimates at 101·0°C by 2·12%, The latter equation (8) overestimates the system O_2–N_2O at 101°C and 180·1°C, but underestimates at other three temperatures. The modified form of Mason-Saxena method shows better agreement with the experiment.

4. Conclusion

There is a good agreement between the theoretical and the experimental values of thermal conductivities of these binary gas mixtures due to these methods like the corresponding methods. It seems that the approximation (equation (6)) taken is valid and the equations (7) and (8) can be used frequently for binary gas mixtures.

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