Int. J. Heat Mass Transfer. Vol. 10, pp.921–929 Pergamon Press Ltd. 1967. Printed in Great Britain

THERMAL CONDUCTIVITY OF BINARY MIXTURES OF SULPHUR DIOXIDE AND INERT GASES

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(*Received* 22 *December* 1966)

Abstract—Thermal conductivity of SO_2–Ar and SO_2–Kr mixtures have been measured for various compositions over the temperature range 39–200·6°C by using the hot-wire method. The observed values are found to vary nonlinearly with composition at all temperatures. An attempt has been made to explain the observed data in the light of Hirschfelder-theory based on local chemical equilibrium assumptions.

NOMENCLATURE

λ_{∞},	thermal conductivity of gas mixture according to Monchick, Pereira and Mason;
λ_{HE},	thermal conductivity of gas mixture according to Hirschfelder–Eucken theory;
$\Delta\lambda$,	inelastic correction term according to Monchick, Pereira and Mason;
ρ_0,	resistance per unit length of the wire at 0°C;
α,	temperature coefficient of resistance of the wire;
J,	mechanical equivalent of heat;
I,	current flowing through the wire [A];
θ,	temperature of the cell wire [°C];
$2l$,	length of the cell wire;
r_1,	radius of the cell wire;
r_2,	internal radius of the cell;
r_3,	external radius of the cell;
K_u,	the apparent thermal conductivity of the gas;
R,	resistance of the wire when current 1 A is flowing through it;
R_0,	resistance of the wire at the bath temperature;
T,	temperature of gas [°C];
λ,	corrected thermal conductivity of the gas [cal/cm s degC];
$(1 - C)$,	cell constant;
$\lambda_{(mon)}$,	thermal conductivity of gas mixture composed of monatomic molecules;
$\lambda_{1(mon)}$,	thermal conductivity of component 1 (i.e. SO_2) without considering the internal degrees of freedom;
$\lambda_{2(mon)}$,	thermal conductivity of component 2 without considering the internal degrees of freedom;
λ_1,	thermal conductivity of component 1 (i.e. SO_2) considering the internal degrees of freedom;
λ_2,	thermal conductivity of component 2 considering the internal degrees of freedom;
x_1,	mole fraction of component 1 (i.e. SO_2);
x_2,	mole fraction of component 2;
$\varepsilon_{12/k}$, σ_{12},	force parameters for unlike interactions.

INTRODUCTION

THE PROBLEM of heat transfer in monatomic as well as polyatomic gas mixtures has aroused considerable interest amongst various workers in recent years. In addition to its importance from the theoretical point of view, very accurate knowledge of thermal conductivity of gases under extreme conditions is necessary for technical as well as industrial advances.

Although several workers have tried to extend the classical theory [1] to the case of gas mixtures it has been found to be adequate only for monatomic gases. The problem of heat transfer in polyatomic gases and their mixtures is much more complicated but quite interesting, since in this case the exchange of energies between translational and various internal degrees of freedom must occur. The first attempt to take into consideration all these effects was made by Eucken. Several workers [2–5] have later on modified Eucken's theory but the observed values of thermal conductivity of polyatomic (polar as well as nonpolar) gases are always found to be low compared to the theoretical values. Mason and Monchick [6] have recently derived explicit expressions for thermal conductivity of polar and nonpolar polyatomic gases starting from the semiclassical theories of Wang–Chang and Uhlenbeck [7] and of Taxman [8] in deriving the expressions for thermal conductivity they assumed that for nonpolar polyatomic gases relaxation of energy transfer between translational and internal degrees of freedom is important, while for polar gases a second effect namely resonant exchange of energy is to be considered.

The theoretical treatment of polyatomic gas mixtures (polar–polar or polar–nonpolar) becomes much more complicated since in such cases accurate knowledge about the interactions amongst different species is required. Although various empirical formulae [9] have been suggested by several workers, the first attempt to formulate a rigorous theory was made by Hirschfelder [10]. In deriving expressions for thermal conductivity he assumed that all exchanges, e.g. rotational–translational or vibrational–translational, are fast enough so that at all points the condition of local chemical equilibrium holds good. Several workers [11–13] have found that this theory, when applied to nonpolar polyatomic and monatomic gas mixtures, yields fairly good results. For gas mixtures involving polar components no rigorous theory has been formulated so far. Recently Monchick, Pereira and Mason [14] have extended their formulations for pure polar and nonpolar polyatomic gases to the case of mixtures. According to them the thermal conductivity λ_∞ of a gas mixture is well represented by,

$$\lambda_\infty = \lambda_{HE} + \Delta\lambda \tag{1}$$

where λ_{HE} is the thermal conductivity of the mixture obtained by Hirschfelder–Eucken formulation and $\Delta\lambda$ is a correction term involving inelastic collision numbers. Monchick *et al.* [14] have observed that the correction term $\Delta\lambda$ is very small for mixtures of nonpolar and nonpolar–polar gases. Hence in such cases the original Hirschfelder–Eucken theory is assumed to be applicable.

In the present work the thermal conductivities of binary mixtures of sulphur dioxide with inert gases argon and krypton have been measured over the temperature range 39–200·6°C. Since the correction term $\Delta\lambda$ is expected to be very small, an attempt has been made to interpret the present data with the help of Hirschfelder–Eucken theory.

THEORY AND FORMULAE

The complete theory of the thick-wire variant of the hot-wire method has been worked out in detail by Kannuluik and Martin [15] and Kannuluik and Carman [16]. It takes into account the actual distribution of temperature in the wire and the ambient gas subject to the boundary condition that both ends of the wire and the wall of the tube are always kept at the same temperature, which for convenience is taken as an arbitrary zero. It is, however, more convenient to assume a strictly radial flow at heat from the wire surface and thereafter to apply a correction for the slight axial flow at the ends. With the assumption of radial flow the differential equation for the steady flow of heat is

$$\pi r_1^2 \lambda \frac{d^2\theta}{dz^2} + 2\pi r_1 h\theta + \frac{I^2\rho_0(1 + \propto\theta)}{J} = 0 \quad (2)$$

where

$$h = K_u/r_1 \ln(r_2/r_1) \quad (3)$$

and λ, K_u are respectively the thermal conductivities of the wire and the gas, r_1, r_2 the radius of the wire and internal radius of the tube respectively, ρ_0 is the resistance per unit length of the wire at 0°C, α the temperature coefficient of resistance of the wire and J the mechanical equivalent of heat. The solution of equation (2) is

$$f(\beta l) = \frac{1}{(\beta l)^2}\left(1 - \frac{\tan h\beta l}{\beta l}\right) = \frac{2\pi r_1^2 \lambda J(R - R_0)}{R_0^2 I^2 \alpha l}$$

with (4)

$$\beta^2 = \frac{2h}{r_1\lambda} - \frac{I^2 R_0 \alpha}{2\pi r_1^2 \lambda J l}$$

where R is the resistance of the wire when a current 1 A is flowing, R_0 is the resistance at the bath temperature, i.e. for $I = 0$, $2l$ is the length of the cell wire.

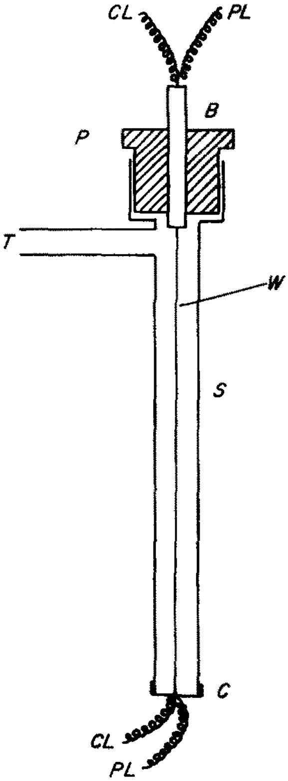

FIG. 1. Thermal conductivity cell.

P = teflon plug,
S = steel tube,
PL = potential leads,
B = brass pin,
C = brass cap,
CL = current leads,
W = platinum wire,
T = gas inlet.

DESCRIPTION OF THE APPARATUS

The conductivity cell was specially designed for use over a wide range of temperature and was similar to that used by Srivastava and Das Gupta [17]. A platinum wire 6·29-cm long and nearly 0·1 cm in diameter was mounted along the axis of a thin walled metal tube approximately 0·6 cm in diameter and made out of a stainless steel rod. The bore of the cell was uniform to one thousandth of an inch over the entire effective length. The method of electrically insulating the wire from the tube has been shown in Fig. 1. A hard setting araldite supplied by Messrs. Ciba of India Ltd., was used for vacuum as well as glass to metal sealing. The conductivity cell was kept immersed in a high temperature thermostatic oil bath (supplied by Messrs. Townson and Mercer Ltd., England). The oil used in the bath was of the type Shell Valvata 85, having a flash point above 250°C. Effective stirring in conjunction with the automatic temperature control system provided with the bath enables the bath temperature to be kept constant within ±0·05 degC. A Pye precision vernier potentiometer reading up to 1 μV was used for the measurement of small change in the resistance of the cell wire with the change of composition of gas mixtures. The geometrical constants of the cell, viz. the length and diameter of the cell wire and the internal radius of the tube were first determined very accurately. The values of the cell constants are recorded in Table 1. The gas mixtures were prepared with the help of a gas mixing unit and

Table 1. Constants of the thermal conductivity cell at different temperatures

Constants	Temperature (°C) 39	80	120·7	160·5	200·5
Thermal conductivity λ of the wire (cal/cm degC)	0·1670	0·1703	0·1731	0·1748	0·1756
Temperature coefficient α of the platinum wire (°C^{-1})	0·00300	0·00264	0·00238	0·00217	0·00200
Resistance of the cell wire (Ω)	0·9706	1·0926	1·2089	1·3250	1·4406
Cell constant $(1 - C)$	0·987	0·985	0·986	0·983	0·983

Length of the wire ($2l$): 6·290 cm.
Radius of the wire (r_1): 0·00506 cm.
Internal diameter of the tube ($2r_2$): 0·301 cm.
Outer diameter of the tube ($2r_3$): 0·590 cm.

the compositions were determined by applying the law of partial pressures.

EXPERIMENTAL RESULTS

For determining R_0, the resistance uf the cell wire when the current $I = 0$ the cell was highly evacuated and the resistance R of the cell–wire was measured for different currents I. $1/R$ was then plotted against I^2 and R_0 was obtained by extrapolation to zero current. In this way R_0 was determined at the temperatures under consideration. The temperature coefficient of resistance α was then determined plotting R_0 against temperature and using the relation $\alpha = (1/R_0)\, dR_0/dt$. For the sake of illustration observations taken for the binary mixtures SO_2–Ar at 80·1°C are recorded in Table 2. In this table x_1 is the mole fraction of SO_2, K_u the apparent thermal conductivity of mixture calculated from equations (3) and (4) and K' is that obtained after reduction to bath temperature and making corrections for non-radial flow, radiation loss, temperature jump and wall effects. λ is the thermal conductivity obtained after correcting the mean values of K' for the asymmetry in the cell construction by the relation $\lambda = K'(1 - C)$. The factor $(1 - C)$ was obtained by calibrating the cell with neon at 39, 80, 120·7, 160·5 and 200·5°C and taking the data of Kanniluik and Carman [16] as standard. Since the different values of $(1 - C)$ showed no systematic change with temperature the average value of $(1 - C)$ has been used throughout the entire temperature range.

Gaseous sulphur dioxide used in this experiment has been prepared by the action of concentrated sulphuric acid on sodium sulphite. The gas has been properly dried before use by passing it through calcium chloride. The inert gases used were supplied by Messrs. British Oxygen Co., England. The data thus obtained have been recorded in column 3 of the Tables 3 and 4. It is found that the observed conductivity of pure SO_2 is higher than the values given by Baker and De Haas [18] and lower than that obtained by El Nadi and Salam [19].

The composition dependence of thermal conductivity are shown graphically in Figs. 2 and 3 along with the theoretically computed values.

COMPARISON WITH THEORY

By extending the method employed in the case of pure polyatomic gases Hirschfelder [10] has obtained the following expression for

Table 2. Thermal conductivity of SO_2–Ar *at* 80·1°C (cal/cm s degC)

Mole fraction of SO_2 (x_1)	I (mA)	$(R - R_0)$ (Ω)	$K_u \times 10^5$	$K' \times 10^5$	$K'_{mean} \times 10^5$	$\lambda \times 10^5$
	128·37	0·01930	4·975	4·877		
0·0	129·38	0·01958	4·983	4·884	4·878	4·854
	130·22	0·01988	4·973	4·872		
	128·21	0·02108	4·525	4·442		
0·151	129·27	0·02136	4·542	4·458	4·441	4·419
	130·56	0·02196	4·509	4·423		
	128·42	0·02199	4·343	4·252		
0·280	129·41	0·02231	4·350	4·258	4·254	4·233
	130·91	0·02286	4·345	4·251		
	130·95	0·02522	3·923	3·822		
0·504	129·83	0·02489	3·905	3·805	3·817	3·798
	128·55	0·02429	3·923	3·825		
	128·52	0·02828	3·343	3·235		
0·790	129·68	0·02880	3·343	3·233	3·230	3·214
	131·07	0·02955	3·333	3·221		
	130·03	0·03178	3·032	2·908		
1·000	129·29	0·03142	3·031	2·908	2·908	2·893
	128·25	0·03092	3·030	2·909		

the thermal conductivity of a binary mixture,

$$\lambda_\infty = \lambda_{(mon)} + \frac{\lambda_1 - \lambda_{1(mon)}}{1 + x_2/x_1 \,.\, D_{11}/D_{12}} + \frac{\lambda_2 - \lambda_{2(mon)}}{1 + x_1/x_2 \,.\, D_{22}/D_{12}} \qquad (5)$$

where $\lambda_{(mon)}$ is the thermal conductivity when the gas mixture is supposed to be composed of monatomic molecules. λ_1, λ_2 are the thermal conductivities; D_{11}, D_{22} are the self-diffusion coefficients and x_1, x_2 are the mole fractions of the components 1 and 2 of the mixture. D_{12} represents the mutual diffusion coefficients. Since in the present case one of the components is monatomic the equation (5) reduces to

$$\lambda_\infty = \lambda_{(mon)} + \frac{\lambda_1 - \lambda_{1(mon)}}{1 + x_2/x_1 \,.\, D_{11}/D_{12}}. \qquad (6)$$

In the present case the theoretical calculations have been done in two ways. Firstly in both the

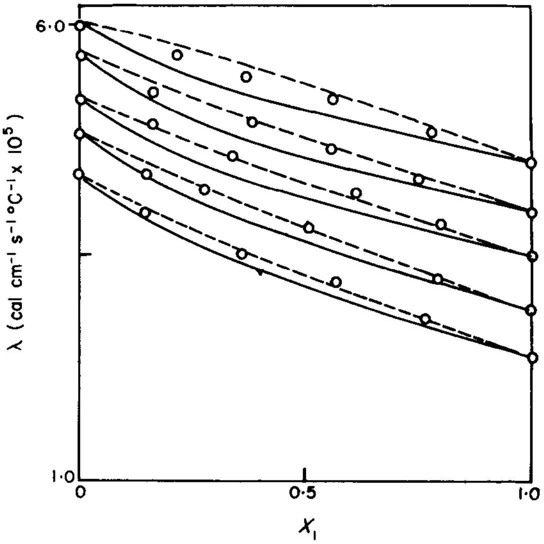

FIG. 2. Thermal conductivity of SO_2–Ar mixtures.
⊙ experimental points,
—— calculated values (from combination rules),
– – – calculated values (from binary viscosity data).

Table 3. Thermal conductivity of SO_2–Ar *mixtures at different temperatures* (cal/cm s degC)

T °C	Mole fraction of SO_2 (x_1)	$\lambda_{expt} \times 10^5$	$\lambda_{calc} \times 10^5$ (from combination rules)	$\lambda_{calc} \times 10^5$ (from binary viscosity data)
39·0	0·0	4·389	4·389	4·389
	0·146	3·995	3·929	4·009
	0·362	3·533	3·435	3·531
	0·572	3·228	3·080	3·126
	0·764	2·810	2·746	2·798
	1·000	2·374	2·374	2·374
80·1	0·0	4·854	4·854	4·854
	0·151	4·419	4·351	4·423
	0·280	4·233	4·103	4·307
	0·504	3·798	3·662	3·774
	0·790	3·214	3·212	3·268
	1·000	2·893	2·893	2·893
121·3	0·0	5·220	5·220	5·220
	0·166	4·964	4·810	4·920
	0·344	4·609	4·442	4·590
	0·608	4·171	3·992	4·108
	0·798	3·838	3·719	3·787
	1·000	3·511	3·511	3·511
161·1	0·0	5·699	5·699	5·699
	0·164	5·300	5·191	5·367
	0·381	4·982	4·774	5·014
	0·556	4·684	4·508	4·720
	0·750	4·337	4·271	4·403
	1·000	3·989	3·989	3·989
200·6	0·0	6·047	6·047	6·047
	0·215	5·698	5·545	5·753
	0·373	5·479	5·291	5·537
	0·558	5·220	5·046	5·262
	0·782	4·848	4·804	4·926
	1·000	4·530	4·530	4·530

cases the unlike interaction terms have been calculated using the force parameters obtained from viscosity data and using the usual combination rules, for polar–nonpolar systems. Secondly in the case of SO_2–Kr the force parameters ($\varepsilon_{12}/k = 244$°K; $\sigma_{12} = 3{\cdot}808$ Å) determined from diffusion data [20] have been used while for SO_2–Ar system since no reliable diffusion data are available, parameters ($\varepsilon_{12}/k = 280$°K; $\sigma_{12} = 3{\cdot}392$ Å) determined from binary viscosity data [21] have been utilized. In both the cases pure component thermal conductivity occurring in equation (6) has been replaced by experimentally determined values. The theoretically computed results thus obtained have been recorded in columns 4 and 5 of the Tables 3 and 4 and plotted along with the experimental results in Figs. 2 and 3.

DISCUSSION

The present analysis shows that although the experimental results are generally higher than the theoretically calculated values, Hirschfelder–Eucken theory can at least qualitatively explain the composition dependence of the thermal conductivity. In the case of SO_2–Kr system better agreement between theoretical and experimental values is observed at low temperature when unlike force parameters determined from diffusion data are used. The

Table 4. Thermal conductivity of SO_2*–Kr mixtures at different temperatures* (cal/cm s degC)

T °C	Mole fraction of SO_2 (x_1)	$\lambda_{expt} \times 10^5$	$\lambda_{calc} \times 10^5$ (from combination rules)	$\lambda_{calc} \times 10^5$ (from diffusion data)
39·1	0·0	2·321	2·321	2·321
	0·262	2·389	2·328	2·372
	0·432	2·428	2·350	2·403
	0·624	2·444	2·375	2·415
	0·806	2·458	2·406	2·429
	1·000	2·374	2·374	2·374
80·9	0·0	2·609	2·609	2·609
	0·159	2·694	2·643	2·678
	0·402	2·825	2·725	2·781
	0·592	2·900	2·793	2·844
	0·774	2·931	2·857	2·892
	1·000	2·893	2·893	2·893
121·4	0·0	2·881	2·881	2·881
	0·147	3·070	2·959	2·976
	0·404	3·316	3·119	3·162
	0·613	3·456	3·255	3·286
	0·883	3·505	3·410	3·380
	1·000	3·511	3·511	3·511
161·0	0·0	3·096	3·096	3·096
	0·287	3·495	3·366	3·419
	0·403	3·654	3·477	3·538
	0·598	3·871	3·659	3·713
	0·795	3·950	3·837	3·862
	1·000	3·989	3·989	3·989
200·5	0·0	3·319	3·319	3·319
	0·197	3·683	3·586	3·632
	0·436	4·081	3·906	3·969
	0·657	4·427	4·190	4·242
	0·854	4·605	4·434	4·526
	1·000	4·530	4·530	4·530

agreement is poor at higher temperatures. This may be due to the circumstance that force parameters determined from low temperature diffusion data are not suitable for the calculation of transport coefficient at high temperatures. It is, however, found that poorer agreement between theoretical and experimental results are observed in both the systems studied when force parameters obtained from viscosity data and using usual polar–nonpolar combination rules are utilized for the calculation of unlike interaction term occurring in the Hirschfelder–Eucken formulation.

Hirschfelder, Taylor and Kihara [22] have pointed out that the accurate measurements of viscosity of gaseous mixtures as a function of both temperature and composition can provide a good method for determining the unlike intermolecular forces. The investigations done by Srivastava [23] show that this method when applied to several systems gives very consistent values of unlike force parameters. Consequently in our present investigation we have used the force parameters obtained from viscosity data of SO_2–Ar system for the calculation of unlike interaction terms. It is found that the agree-

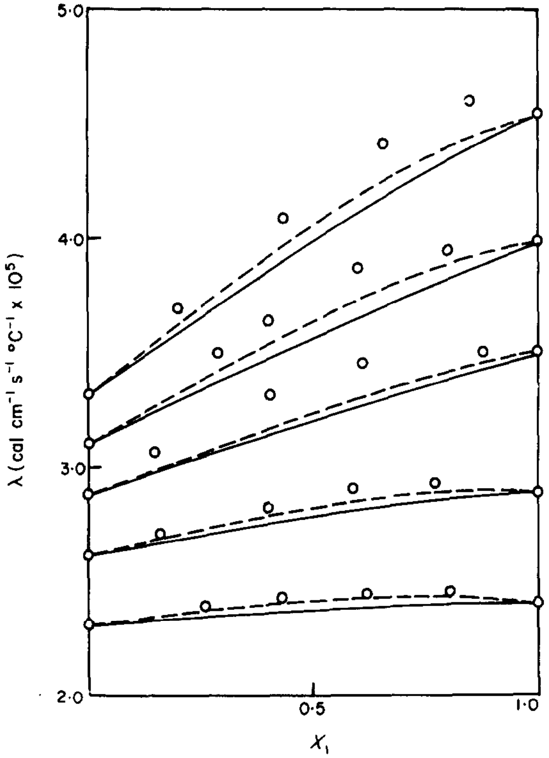

FIG. 3. Thermal conductivity of SO_2–Kr mixtures.
○ experimental points.
—— calculated values (from combination rules).
– – – calculated values (from diffusion data).

ment between the theoretical and experimental results becomes exceedingly good at all temperatures. This shows that the existing semi-empirical combination rules for polar–nonpolar systems are not sufficiently accurate.

ACKNOWLEDGEMENT

The author wishes to thank Prof. B. N. Srivastava, D.Sc., F.N.I., for his guidance and kind interest in the work.

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Résumé—La conductibilité thermique de mélanges de SO_2–Ar et SO_2–Kr ont été mesurées pour différentes compositions dans la gamme de températures 39–200,6°C en employant la méthode du fil chaud. On trouve que les valeurs observées varient d'une façon non-linéaire avec la composition pour toutes les températures. On a essayé d'expliquer les résultats observés à la lumière de la théorie de Hirschfelder basée sur les hypothèses de l'équilibre chimique local.

Zusammenfassung—Die Wärmeleitfähigkeit von SO_2–Ar und SO_2–Kr Gemischen wurde mit der Heizdrahtmethode gemessen. Es wurden verschiedene Konzentrationen im Temperaturbereich von 30 °C bis 200 °C untersucht. Die Leitfähigkeit änderte sich bei allen Temperaturen nichtlinear mit der Konzentration. Es wurde versucht, die Ergebnisse mit Hilfe der Theorie von Hirschfelder, die auf der Annahme örtlichen chemischen Gleichgewichts beruht, zu erklären.

Аннотация—Термоанемометром измерялись коэффициенты теплопроводности смесей SO_2–Ar$_{\text{И}}$ SO_2–Kr для различных химических составов в температурном диапазоне 39–200,6°C.

Найдено, что в данном температурном диапазоне полученые значения нелинейно изменяются с изменением химического состава. Сделана попытка объяснить полученные данные в свете теории Хиршфельдера, основанной на допущениях локального химического равновесия.