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THERMAL CONDUCTIVITY OF NITRIC OXIDE, CARBON MONOXIDE AND THEIR BINARY MIXTURES

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Abstract—Thermal conductivity of the gases nitric oxide, carbon monoxide and their binary mixtures has been measured over the temperature range from 0 to 200°C by the hot-wire method. An attempt has been made to interpret the data in terms of the recent theories of thermal conductivity of polyatomic gases and gas mixtures.

NOMENCLATURE

K,	thermal conductivity of a gas or gas mixture;
M,	molecular weight;
η,	coefficient of viscosity;
C_v,	heat capacity at constant volume;
f_{ME},	modified Eucken factor;
ρ,	density;
R,	universal gas constant;
D,	diffusion coefficient;
f_{MM},	modified Eucken factor obtained by Mason and Monchick;
C_{rot},	heat capacity of the rotational degrees of freedom;
Z_{rot},	collision number for rotational relaxation;
$C_{v\,trans}$,	heat capacity due to translational degrees of freedom;
C_{int},	heat capacity due to internal degrees of freedom;
C_K,	heat capacity of the Kth internal mode;
Z_K,	collision number for the kth mode;
K_H,	calculated value of thermal conductivity of a binary mixture from Hirschfelder's theory;
$K_{\text{mix-mon}}$,	calculated value of the thermal conductivity of the mixture where the gases are treated as monatomic;
K_1,	calculated value of the thermal conductivity of the first component of the binary mixture of gases;
K_2,	calculated value of the thermal conductivity of the second component of the binary mixture of gases;
$K_{1\,mon}$,	calculated value of the thermal conductivity of component 1 without considering the internal degrees of freedom;
$K_{2\,mon}$,	calculated value of the thermal conductivity of component 2 without considering the internal degrees of freedom;
x_1,	molefraction of component 1;
x_2,	molefraction of component 2;
D_{11},	self diffusion coefficient of component 1;
D_{22},	self diffusion coefficient of component 2;
D_{12},	mutual diffusion coefficient;
K_{MPM},	calculated value of the thermal

conductivity of the mixture according to the theory of Mason, Pereira and Monchick;

ΔK, inelastic correction term according to Monchick, Pereira and Mason;

$\mathscr{L}_{qq}^{rs,r's'}$, $\mathscr{L}_{qq'}^{rs,r's'}$ matrix elements of the collision operators that come out of Chapman–Enskog solution of the Boltzmann equation;

$\Lambda_{\alpha\beta}$, $\delta_{q\alpha}$, $\ell_{qq}^{rs,r's'}$, defined in [3].

1. INTRODUCTION

THE PROBLEM of heat conductivity of polyatomic gases is complicated due to the relaxation effects in the energy transfer process between the various degrees of freedom. In recent years Mason and Monchick [1, 2] and Monchick, Pereira and Mason [3] have made significant advance in this regard by reducing the semiclassical treatment of Wang Chang and Uhlenbeck [4] and de Boer [5] to a tractable form with the help of some simplifying assumptions. With the availability of more advanced theories the precise measurement of thermal conductivity of polyatomic gases and gas mixtures has assumed great importance. In view of this necessity, a number of such measurements [6–13] for several polar and non-polar gases and binary mixtures of polyatomic gases have been made. However, one of the more common gases which has been found to behave in an apparently anomalous manner is nitric oxide [1]. Carbon monoxide is similar to nitric oxide in many respects and a parallel measurement of thermal conductivity of this gas with that of nitric oxide is likely to yield valuable information regarding the anomalous behaviour of nitric oxide. The thermal conductivities of nitric oxide and carbon monoxide being very close the mixture conductivity of these two gases is likely to be affected significantly by cross-relaxation phenomena. Consequently, we have thought it desirable to measure thermal conductivity of nitric oxide and carbon monoxide and their mixtures over a range of temperatures by a precise technique.

In this paper the results of our measurement of the thermal conductivity of nitric oxide, carbon monoxide and their mixtures over a temperature range from 0 to 200°C have been reported. Attempts have been made to interpret these data in terms of the recent theory for thermal conductivity of polyatomic gases and their mixtures [3].

2. EXPERIMENTAL

The hot-wire cells used for thermal conductivity measurements were similar in design to that of Das Gupta [6]. In the whole temperature range two cells were used. For the temperature range 80–200°C an oil bath and at 0°C a kerosene oil bath with Freon compressor was used. The theory of the thick-wire variant of the hot-wire method and the procedure followed by us have been described in a number of previous publications [11, 12]. The thermal conductivity cells were standardised by spectroscopically pure Argon gas (supplied by the British Oxygen Co., U.K.). The gases were prepared by standard laboratory procedures [14] and the purity of these gases was tested by a mass spectrometer (Associated Electrical Industries, MS3 model). The gas mixtures were prepared in a suitable gas mixing unit. In general, our temperature control was within ±0·02°C and the accuracy of the thermal conductivity data should be within 1 per cent for the pure gases and 1–2 per cent for the mixtures. The measured thermal

Table 1. Thermal conductivity of nitric oxide and carbon monoxide at different temperatures

Substance	Temperature (°C)	$K_{expt} \times 10^5$ cal.°C^{-1} (cm^{-1}.s^{-1})	$K \times 10^5$ cal.°C^{-1} (cm^{-1}.s^{-1})	Z_{rot}
NO	0	5·61	6·16	2·8
	80	7·14	7·52	2·8
	120	7·68	8·19	3·3
	160	8·37	8·84	4·9
	200	9·15	9·52	8·8
CO	0	5·50	5·94	1·4
	80	6·82	7·27	2·9
	120	7·60	7·90	3·8
	160	8·22	8·52	4·4
	200	8·61	9·13	5·9

conductivity values after correction for radiation loss, temperature jump effect, cell asymmetry, reduction to bath temperature etc. are shown in Table 1 for pure gases and in Table 2 for the binary mixtures. In our measurements the gas pressure was kept below 7–8 cm of Hg to avoid convection effect.

The agreement of our thermal conductivity data for nitric oxide with those of Johnston and Grilly [15] and Choy and Raw [16] in the temperature where comparison is possible is within the experimental error. The same conclusion holds for carbon monoxide.

3. INTERPRETATION OF THE DATA

(a) *Pure components: nitric oxide and carbon monoxide*

In order to interpret thermal conductivity of polyatomic gases, Ubbelohde [17] made the

Table 2. Thermal conductivity of the mixture NO–CO *at different temperatures*
(*Results have been expressed in* cal. °C^{-1} . cm^{-1} . s^{-1})

Temperature (°C)	Mole fraction of NO x_1	$K_{expt} \times 10^5$	$K_{calc} \times 10^5$ from equation (4)	$K_{calc} \times 10^5$ from equation 4) (using expt. values of K_1 and K_2)	$\Delta K \times 10^5$ from (equation 6)	$K_{MPM} \times 10^5$ from equation (5)
0	0·000	5·50	5·94	5·50	0·00	5·50
	0·067	5·38	5·95	5·51	0·01	5·52
	0·246	5·44	5·99	5·53	0·03	5·56
	0·496	5·50	6·04	5·55	0·05	5·60
	0·741	5·56	6·10	5·58	0·05	5·63
	0·959	5·60	6·15	5·60	0·04	5·64
	1·000	5·61	6·16	5·61	0·00	5·61
80	0·000	6·82	7·27	6·82	0·00	6·82
	0·052	6·79	7·28	6·84	0·01	6·85
	0·246	6·88	7·33	6·90	0·02	6·92
	0·501	6·93	7·39	6·98	0·03	7·01
	0·752	7·03	7·46	7·06	0·04	7·10
	0·949	7·19	7·51	7·12	0·04	7·16
	1·000	7·14	7·52	7·14	0·00	7·14
120	0·000	7·60	7·90	7·60	0·00	7·60
	0·058	7·56	7·92	7·60	0·01	7·61
	0·273	7·70	7·98	7·62	0·02	7·64
	0·506	7·80	8·04	7·64	0·03	7·67
	0·739	7·82	8·11	7·65	0·03	7·68
	0·948	7·83	8·18	7·68	0·03	7·71
	1·000	7·68	8·19	7·68	0·00	7·68
160	0·000	8·22	8·52	8·22	0·00	8·22
	0·050	8·13	8·53	8·23	0·02	8·25
	0·499	8·44	8·68	8·29	0·03	8·32
	0·744	8·54	8·76	8·33	0·03	8·36
	0·942	8·40	8·82	8·36	0·02	8·38
	1·000	8·37	8·84	8·37	0·00	8·37
200	0·000	8·61	9·13	8·61	0·00	8·61
	0·057	8·51	9·07	8·56	0·02	8·58
	0·255	8·74	9·22	8·74	0·03	8·77
	0·504	9·12	9·25	8·82	0·02	8·84
	0·734	9·20	9·41	9·00	0·02	9·02
	0·947	9·35	9·50	9·12	0·05	9·17
	1·000	9·15	9·52	9·15	0·00	9·15

first significant advance from the intuitive approach of Eucken by considering molecules in different quantum states to be separate chemical species which are in local chemical equilibrium. Hirschfelder [18], following the idea of Ubbelohde derived the modified Eucken expression on a more rigorous basis which can be written as,

$$\frac{KM}{\eta C_v} = f_{ME} = \frac{\rho D}{\eta} + \frac{3}{2}\left[\frac{5}{2} - \frac{\rho D}{\eta}\right]\left(\frac{R}{C_v}\right) \qquad (1)$$

where K is the thermal conductivity, M the molecular weight, D the diffusion coefficient and ρ the density.

However, for most of the polyatomic gases, the relaxation of internal energy has to be considered which is a difficult problem. Recently some progress in this regard has been made by Mason and Monchick [1] who have reduced the formulation of Wang Chang and Uhlenbeck [4] and de Boer [5] to a tractable form by making a number of well-defined approximations. This treatment, to the first approximation, reduces to the modified-Eucken expression. The relaxation effects are taken into account in the second approximation which can be written for translational-rotational energy transfer as,

$$f_{MM} = \frac{\rho D}{\eta} + \frac{3}{2}\left(\frac{5}{2} - \frac{\rho D}{\eta}\right)\left(\frac{R}{C_v}\right) - \frac{2}{\pi C_v}\left(\frac{5}{2} - \frac{\rho D}{\eta}\right)^2 \frac{C_{\text{rot}}}{Z_{\text{rot}}} \qquad (2)$$

where Z_{rot} is the collision number for rotational relaxation and C_{rot} is the contribution of rotational degrees of freedom to the heat capacity.

For other degrees of freedom Mason and Monchick [1] have suggested the following expression for f for nonpolar polyatomic gases:

$$f = \frac{1}{C_v}\left[\frac{5}{2} C_{v\,\text{trans}} + \frac{\rho D}{\eta} C_{\text{int}} - \frac{2}{\pi}\left(\frac{5}{2} - \frac{\rho D}{\eta}\right)^2 \sum_k \frac{C_k}{Z_k}\right] \qquad (3)$$

where C_k is the heat capacity of the kth internal mode and Z_k the corresponding collision number for relaxation.

In the temperature range of our measurements it is possible to neglect vibrational energy transfer. However, for nitric oxide due to the low lying electronic state the possibility of electronic energy transfer is present. Recent measurement for nitric oxide [19] shows Z_{elec} to be 70 and as given in equation (3), electronic energy transfer cannot probably play a significant role for such a high value of Z_{elec}. No reliable measurement of Z_{rot} for nitric oxide and carbon monoxide is available. Consequently, we have calculated Z_{rot} from equation (2) using smoothed out experimental thermal conductivity data. For this purpose the viscosity data were taken from [20]. The heat capacity data used for nitric oxide were those obtained by Johnston and Chapman [21] and for carbon monoxide the data were taken from [22]. The values of Z_{rot} thus obtained are shown in column 5 of Table 1. It may be seen that the Z_{rot} values obtained for nitric oxide and carbon monoxide are quite reasonable in view of the similarity of these molecules with nitrogen and oxygen. Consequently, it is possible to represent thermal conductivity data of these gases by taking a suitable temperature dependence of Z_{rot}. Our calculations also show a steeper rise of Z_{rot} with temperature than that given by Parker's theory [23] which is applicable strictly to homonuclear diatomic molecules only.

It is relevant here to point out that another factor which can influence thermal conductivity of nitric oxide at low temperatures is dimerization due to the free electron. Recently several methods for the calculation of percentage of dimers have been proposed [24, 25]. The presence of dimers also brings in the question of heat transfer by chemical reaction [26] which is a rather complicated problem. However, sample calculations show that in the temperature and pressure range of our measurements, dimerization cannot play any significant role.

(b) *Binary mixtures*

Hirschfelder [27] extended his treatment for pure polyatomic gases to mixtures which for a binary mixture can be written as

$$K_H = K_{\text{mix-mon}} + [K_1 - K_{1\,\text{mon}}] \times \left[1 + \left(\frac{x_2}{x_1}\right)\left(\frac{D_{11}}{D_{12}}\right)\right]^{-1} + [K_2 - K_{2\,\text{mon}}] \times \left[1 + \left(\frac{x_1}{x_2}\right)\left(\frac{D_{22}}{D_{12}}\right)\right]^{-1} \tag{4}$$

where $K_{\text{mix-mon}}$ is the thermal conductivity of the mixture where the gases are treated as monatomic, x's the mole fractions and D's the diffusion coefficient.

Monchick, Pereira and Mason [3] have also extended the treatment of Monchick and Mason [1] to the case of polyatomic gases which includes the effects of relaxation of internal energy on thermal conductivity. This treatment as for the pure gases, reduces to K_H of equation (4) in the first approximation. The actual formula for the mixture can be written as

$$K_{MPM} = K_H + \Delta K \tag{5}$$

where

$$\begin{aligned}\Delta K = 4\sum_q \Big\{ x_q \sum_\alpha \Lambda_{q\alpha} \sum_\beta (\Delta\,\mathscr{L}_{\alpha\beta}^{01,\,10})\Big(\sum_\gamma \Lambda_{\beta\gamma} x_\gamma\Big) \\ -2\left(\frac{x_q}{\mathscr{L}_{qq}^{01,\,01}}\right)\sum_\alpha (\Delta \mathscr{L}_{q\alpha}^{10,\,01})\Big(\sum_\beta \Lambda_{\alpha\beta} x_\beta\Big) \\ -\left(\frac{x_q^2}{\mathscr{L}_{qq}^{01,01}}\right)\Bigg[\left(\frac{\ell_{qq}^{01,01}}{\ell_{qq}^{10,10}}\right)\left(\frac{\Delta\ell_{qq}^{10,10}}{\ell_{qq}^{10,10}}\right) \\ +2\left(\frac{\Delta\ell_{qq}^{10,01}}{\ell_{qq}^{10,10}}\right) + \left(\frac{\Delta\ell_{qq}^{01,01}}{\ell_{qq}^{01,01}}\right) - \left(\frac{\Delta\ell_{qq}^{01,01}}{\mathscr{L}_{qq}^{01,01}}\right)\Bigg]\Big\}\end{aligned} \tag{6}$$

where

$$\ell_{qq}^{rs,\,r's'} = \lim_{x_q \to 1} \mathscr{L}_{qq}^{rs,\,r's'}$$

and

$$\Lambda_{\alpha\beta} = \left|\begin{array}{c|c} \mathscr{L}_{qq'}^{10,\,10} & \delta_{q\alpha} \\ \hline \delta_{\beta q'} & 0 \end{array}\right| \left|\mathscr{L}_{qq'}^{10,\,10}\right|^{-1}.$$

$\mathscr{L}_{qq}^{rs,\,r's'}$, $\mathscr{L}_{qq'}^{rs,\,r's'}$ are the matrix elements of the collision operators that come out of the Chapman–Enskog solution of the Boltzmann equation. The expressions for these elements have been given by Monchick *et al.* [3]. The correction term ΔK vanishes as the molefraction $x_q \to 1$.

In column 4 of the Table 2 we have given the calculated values of thermal conductivity of the mixtures using equation (4) and in column 5 of the same table are shown the values calculated from equation (4) using the experimental values of K_1 and K_2. The values of ΔK have been given in the sixth column of the said table. The theoretical calculations were performed on the Lennard-Jones (12:6) potential and the unlike interactions were approximated by the usual combination rules.

A close inspection of the experimental data given in column 3 of the Table 2 will reveal two important features: (i) slight lowering (usually ~1 per cent) in the value of the thermal conductivity at the lower concentrations of the component (NO) having higher conductivity; (ii) occurrence of a hump at the higher concentrations of the same component.

The initial lowering in the mixture conductivity at the lower concentrations of the component having higher conductivity was observed in the binary systems H_2–He, N_2-A and O_2–A by Mukhopadhyay and Barua [11, 12]. The magnitude of lowering in the system NO–CO is small. However, the occurrence of lowering in the mixture conductivity at all the temperatures reasonably rules out the possibility of attributing this lowering to experimental error. It may also be seen that the Hirschfelder–Eucken formula cannot explain the occurrence of a lowering and a hump in thermal conductivity vs. composition curves even when experimental conductivities of the pure components are used to calculate mixture conductivities. However, by using equation (5) which considers cross-relaxation as well the appearance of the hump at least can be explained qualitatively (column 7, Table 2). This result should be considered as gratifying in view of the various approximations made in deriving equation (6) and the uncertainties in the relaxation times. The failure of equation (5) at 200°C to reproduce the hump in the thermal conductivity vs. composition curve can be attributed to the unusual Z_{rot} values obtained for nitric oxide at that temperature.

CONCLUSIONS

The results obtained show that thermal conductivity of nitric oxide and carbon monoxide can be explained satisfactorily by the Mason and Monchick's theory. For the binary mixtures the theory of Monchick, Pereira and Mason has been found to be partially successful. Direct determination of Z_{12} values as a function of temperature is essential for a more adequate test of the theory.

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Résumé—Les conductivités thermiques de l'oxyde nitrique et de l'oxyde de carbone gazeux ainsi que de leurs mélanges binaires ont été mesurées dans la gamme de température allant de 0 à 200°C par la méthode du fil chaud. Une tentative a été faite pour interpréter les résultats à l'aide des théories récentes de la conductivité thermique des gaz polyatomiques et des mélanges gazeux.

Zusammenfassung—Nach der Hitzdrahtmethode wurde die Wärmeleitfähigkeit von Stickoxyd, Kohlenmonoxyd und ihren binären Gemischen im Temperaturbereich 0 bis 200°C gemessen. Es wurde versucht, die Daten auf Grund der neueren Theorien der Wärmeleitfähigkeit vielatomiger Gase und Gasgemische zu interpretieren.

Аннотация—Теплопроводность газовой двуокиси натрия, окиси углерода и их бинарных смесей измерена в диапазоне температур от 0 до 200°C методом горячей проволоки. Сделана попытка выразить данные в свете новых теорий теплопроводности полиатомых газов и газовых смесей.