THERMAL CONDUCTIVITY OF THE SLOWLY REACTING SYSTEM $2HI \leftrightharpoons H_2+I_2$

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ABSTRACT. The thermal conductivity of the dissociating system $2HI \leftrightharpoons H_2+I_2$ has been measured between 175°C and 205°C at a pressure below 1 atm. The absolute hot-wire method and an all-glass apparatus with a glass diaphragm manometer has been employed. The experimental conductivity values have been compared with the values calculated from the theoretical expression developed by Srivastava *et al.* for a slowly reacting system. Fair agreement has been obtained between the experimental and the calculated values.

INTRODUCTION

The study of the thermal conductivity of chemically reacting gaseous systems is of considerable interest both from the theoretical and the experimental point of view. Several workers (Hirschfelder, 1957a; Butler and Brokaw, 1957) have investigated this problem theoretically assuming the condition of local chemical equilibrium to hold. However, the experimental investigations with different reacting systems (Coffin, 1959; Srivastava and Barua, 1961; Barua and Chakraborti, 1962) have proved the inadequacy of the local equilibrium theory. This is due to the fact that the reaction rate for almost all chemical reactions are not fast enough to maintain the condition of local chemical equilibrium. The problem of non-equilibrium heat transfer in reacting gases has been considered theoretically by Franck and Spalthoff (1954); Secrest and Hirschfelder (1961) and Brokaw (1961).

Secrest and Hirschfelder (1961) have considered two types of chemical reactions, viz : (1) Moderately fast reactions and (2) slow reactions. Srivastava, Barua and Chakraborti (1963) have attempted to interpret the experimental heat conductivity data (Barua and Chakraborti, 1962) for the system $2NO_2 \leftrightharpoons 2NO+O_2$ by extending the theory of Secrest and Hirschfelder (1961) for slowly reacting systems.

In the present paper we have reported the thermal conductivity of dissociating hydrogen iodide, the reaction rate for which is known to be slow (Sullivan, 1959). The experimental values have been compared with the values calculated on the basis of the expressions developed by Srivastava, Barua and Chakraborti (1963).

PREPARATION OF HYDROGEN IODIDE

Pure HI was obtained by the action of water on a mixture of red phosphorus and re-sublimed iodine according to the reaction

$$2P + 3I_2 = 2PI_3$$

$$2PI_3 + 6H_2O = 2H_3PO_3 + 6HI$$
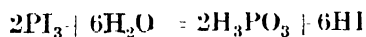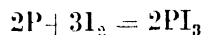
By constructing a suitable glass apparatus, HI was first purified by passing it over moist red phosphorus and P_2O_5 in succession. The purified HI was liquefied in the collecting tube by placing it in an alcohol-liquid oxygen bath. The liquid HI was then solidified by placing the collecting tube in another alcohol-liquid oxygen bath and the system was evacuated. The resulting pure HI was then distilled into ampoules which were sealed off. The ends of the ampoules were made so thin that they could be easily broken by mere tilting.

APPARATUS AND THEORY

The method employed for the thermal conductivity measurements is the thick-wire-variant of the hot-wire method. An all-glass apparatus with a glass diaphragm manometer described earlier in detail has been used to avoid all complications due to spurious chemical reactions. The theory and procedure of the experiment have already been fully described elsewhere (Kannuluik and Carman, 1952; Srivastava and Barua, 1960). The constants of the apparatus at different temperatures are given in Table I.

TABLE I

Constants of the conductivity cell at different temperatures

Constants	Temperature in °C			
	175	185	195	205
Resistance of the cell-wire R_0 in Ω	2.6060	2.6583	2.7116	2.7640
Temperature coefficient of resistance "α" of the platinum wire in °C^{-1}	0.00199	0.00198	0.00192	0.00190
Thermal conductivity "λ" of the platinum wire in cal. cm^{-1}. sec^{-1}. °C^{-1}	0.1748	0.1749	0.1750	0.1752
Cell constant $(1-C)$	0.9788	0.9779	0.9778	0.9775
Length of the cell wire $(2l)$	11.014 cm.			
Radius of the cell wire (r_1)	0.005 cm.			
Internal diameter of the cell $(2r_2)$	0.3220 cm.			
External diameter of the cell $(2r_3)$	0.6021 cm.			

EXPERIMENTAL RESULTS

A typical set of observations taken at 175°C is given in Table II. In the table K_u is the apparent thermal conductivity and K'_u is that obtained after

reduction to the bath temperature. The temperature coefficient of the thermal conductivity of the reacting system was obtained from the values of the thermal conductivity calculated on the basis of the slow reaction theory. K' is the value obtained after correcting for radiation loss, temperature jump and wall effects. K is the thermal conductivity obtained after correcting for the asymmetry in the cell construction by the relation $K = K'(1-C)$. The factor $(1-C)$ was obtained from the measurements of the thermal conductivity of neon by taking the data of Kannuluik and Carman (1952) as standard.

TABLE II

Observations taken for the thermal conductivity K at 175°C
in cal. cm^{-1} . sec^{-1} . °C^{-1}

P in cm. of Hg.	I in mA	$(R-R_0)$ in $m\Omega$	$K_u \times 10^5$	$K'_u \times 10^5$	$K' \times 10^5$	$K \times 10^5$
19.18	105 64	58 00	2 91	2.90	2.89	2.83
25 68	106 55	58 91	2 92	2.91	2.90	2.84
61.46	105 65	57.91	2.82	2.81	2.80	2.74

TABLE III

Experimental and calculated values* of the thermal conductivity of the
system $2HI \rightleftharpoons H_2 + I_2$ expressed in cal. cm^{-1}. sec^{-1} . °C^{-1}

T in °C	P in cm. of Hg.	T_H in °C	T_e in °C	x_2	x_3	$\frac{(1-x_1)}{2}$	K_{expt} $\times 10^5$	K_{cal} $\times 10^5$	$(K_{HI})_{cal}$ $\times 10^5$
	19.18	182.0	178.8			0.0156	2.83	2.57	......
175.0	25.68	181.6	......			......	2.84	......	2.20
	61.46	182.0	......			......	2.74	......	......
	19.42	194.5	......			......	2.92	......	......
185.0	26.46	194.4	189.0			0.0163	2.92	2.63	2.25
	62.60	195.2	......			......	2.96	......	......
	19.54	206.0	......			......	3.00	......	......
195.0	26.69	202.1	198.5			0.0167	3.01	2.73	2.30
	65.01	202.5	......			......	3.02	......	......
	19.81	216.4	210.5			0.0171	3.12	2.85	......
205.0	27.09	216.1	......			......	3.11	......	2.35
	67.45	216.6	......			......	3.12	......	......

*columns 4, 5 and 7 wire calculated for only one value of T corresponding to a T_e value. The values are, therefore, indicated against the particular T_H value.

COMPARISON WITH THEORY

Following the procedure of Srivastava *et. al.* (1963) we get for the slowly reacting system $2HI \rightleftharpoons H_2 + I_2$

$$x_2 x_3 / x_1^2 = \int_{T_H}^{T_c} K_c \frac{k_r}{T^2} \exp[\beta(T_H - T)]dT \Big/ \int_{T_H}^{T_c} \frac{k_r}{T^2} \exp[\beta(T_H - T)]dT \quad \dots \quad (1)$$

where x_1, x_2 and x_3 are the molefractions of HI, H_2, and I_2 respectively, K_c is the equilibrium constant for the hydrogen iodide dissociation, k_r is the rate constant for the reverse reaction $H_2 + I_2 \rightarrow 2HI$, T_H and T_c are the temperatures of the hot and the cold surfaces respectively and β is given by

$$\beta = [2 \ln (r_2/r_1)]/(T_H - T_c), \qquad \dots \quad (2)$$

where r_1 and r_2 are the radii of the cell-wire and the cell respectively.

Further we have the relations

$$x_1 + x_2 + x_3 = 1 \qquad \dots \quad (3)$$

$$x_2 = x_3 = (1 - x_1)/2 \qquad \dots \quad (4)$$

The experimental values of the equilibrium constant K_c at different temperatures are given by Stegmuller (1910). Sullivan (1959) has given the experimental k_r values at different temperatures. The temperature of the hot surface, T_H can be calculated from

$$R_H = R_c\{1 + \alpha(T_H - T_c)\}, \qquad \dots \quad (5)$$

where R_H and R_c are the values of the resistance of the hot wire at T_H and T_c respectively. The values of α and some of the typical values of $(R_H - R_c)$ are given in Table I and Table II respectively.

The thermal conductivity of a chemically reacting gas mixture assuming local chemical equilibrium can be represented as

$$K = K_f + K_R, \qquad \dots \quad (6)$$

where K_R is the contribution of the chemical reaction to the thermal conductivity. For a slowly reacting system K_R is negligible. However, K_f will depend upon the chemical reaction rate as the steady state composition of the gas mixture (given by Eq. (1)) in the cell is dependent on the reaction rate. K_f is given by

$$K_f = K_{mix(mon)} + K_{mix(int)} \qquad \dots \quad (7)$$

$K_{mix(mon)}$ is the thermal conductivity of the mixture when it is assumed to be composed of monatomic molecules only. $K_{mix(int)}$ is the contribution of the internal degrees of freedom. The value of $K_{mix(mon)}$ was calculated to the first

approximation from the expression given by Brokaw (1958) and $K_{mix(int)}$ was calculated from the expression given by Hirschfelder (1957b).

In all our calculations we have used Lennard-Jones (12 : 6) potential model. The force constants for the different components were taken from Hirschfelder, Curtiss and Bird (1954). The steady state composition at any particular temperature is pressure independent and its value was obtained by calculating the integrals in Eq. (1) numerically by using Simpson's one-third rule. The experimental specific heat values were obtained from the standard tables.

The results thus obtained are shown in Table III. Column 5 in the table gives the composition as calculated from Eq. (1) with the help of Eqs. (3) and (4). In column 8 of this table the conductivity values for undissociated hydrogen iodide are given. Comparison of columns (6) and (8) shows that there has been appreciable dissociation. Column 4 represents the temperature to which the composition presented in column 5 would correspond if there were thermodynamical equilibrium. It is to be noted that this temperature is almost equal to the mean of T_c and T_H. To examine this point further, a hypothetical calculation was performed for $T_c = 175°C$ and $T_H = 225°C$. These calculations also showed that the equilibrium temperature was somewhat less than the mean of T_c and T_H. The actual value of T_e was found to be 195 C. Thus the average composition corresponds to a point nearer the colder surface for this cylindrical geometry but for plane geometry Hirschfelder found it to be farther from the cold surface.

CONCLUSIONS

It may be seen from Table III that the experimental values of the thermal conductivity of the system are consistently higher than the calculated values. A part of this discrepancy may be attributed to the effect of the dissociation of molecular iodine. A rough estimate of this effect shows that the contribution due to this may amount to about 3% at the highest temperature.

It should also be mentioned that in the temperature range of our present measurements the dissociation of HI is quite small. Further experiments with this system over a larger range of temperature will be of much interest.

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