Thermal Conductivity of Equilibrated Mixtures of H₂, D₂, and HD

CLARKE C. MINTER and SIGMUND SCHULDINER
U. S. Naval Research Laboratory, Washington, D. C.

The question whether equilibrium is attained in the exchange reaction $H_2 + D_2 \rightleftarrows 2HD$ in a given mixture of electrolytically produced hydrogen and deuterium, could perhaps be decided by measuring the thermal conductivity of mixtures of hydrogen and deuterium before and after equilibrating over a nickel catalyst. The experimentally determined thermal conductivities could then be compared with the conductivities calculated on the assumption that equilibrium is attained.

The thermal conductivity of unequilibrated mixtures of hydrogen and deuterium have been measured by Archer (1), Bolland and Melville (2), and Van Cleave and Maas (8). Unfortunately, the three sets of measurements do not agree, making it necessary to redetermine the conductivities of mixtures of hydrogen and deuterium over the entire range of concentrations.

Farkas and Farkas (4) studied the composition of equilibrated mixtures of H_2, D_2, and HD by carrying out thermal conductivity tests at a pressure of 0.04 mm. of mercury, and found good agreement between observation and calculation based on the classical kinetics value of 4.00 for the equilibrium constant, E, given by

$$E = \frac{[HD]^2}{[H_2] \times [D_2]} \qquad (1)$$

Bolland and Melville (2) assumed a value of 4.00 for E and calculated the compositions for several equilibrated mixtures. These experimental results appear to be out of line with other published measurements of the conductivity of mixtures of hydrogen and deuterium.

Equations derived from kinetic theory for calculating the transport properties of gas mixtures are too complex to be of much use, and in general, do not agree with experiment. However, Buddenburg and Wilke (3) show that an approximation kinetic formula involving an arbitrary constant can be used with fair success for calculating the viscosity of gas mixtures. Lindsay and Bromley (6) obtained fairly good results with the Wassiljewa (9) formula for the thermal conductivity of binary mixtures, but did not apply their equation to ternary mixtures. In this work the thermal conductivity for binary and ternary mixtures of H_2, D_2, and HD must be calculated. The relations developed are ideal in that they involve only the thermal conductivities of the components and their concentrations. Theoretical or approximation equations will not be made for mixtures already in the literature.

EXPERIMENTAL

All measurements of thermal conductivity were carried out at atmospheric pressure and room temperature using the apparatus shown schematically in Figure 1. With this setup the thermal conductivity of the mixture $_0K_M$ in one side of the bridge block can be compared with that of hydrogen by exposing each to two similar filaments of the four-filament bridge. The millivolt output, E, of the bridge can be interpreted in terms of absolute thermal conductivity at 0° C. by means of the equation

$$_0K_M = \frac{1}{\dfrac{1}{_0K_H} - \dfrac{E}{A}} \qquad (2)$$

in which $_0K_H$ is the absolute thermal conductivity of hydrogen at 0° C. and A is the "bridge constant" determined by well-known methods, which involve measuring the bridge output, E, when two pure gases of known absolute thermal conductivity are passed through the two sides of a bridge block, the two gases in this case being hydrogen and helium.

The reason for expressing the observed thermal conductivities in terms of 0° C. should be explained. The bridge operates at room temperature, and the the four small tungsten filaments positioned in cells 3/16 inch in diameter and 1/2 inch deep operate at about 50° C. when carrying 100 ma. in hydrogen. Although approximately 95% of the gas in these cells is only a little above room temperature, the thermal conductivity of the gas is naturally slightly greater than it would be at 0° C. Because the temperature differences are not great and the temperature coefficient of thermal conductivity is practically the same for all the gases involved, the errors resulting from such a procedure are expected to be negligible. Ibbs and Hirst (5) used a similar method for obtaining the absolute thermal conductivities of several gases and found that the results obtained by operating at the higher temperature were in the same proportion as those at 0° C.

The experimental procedure consisted in filling the system with either hydrogen or deuterium between points A and B of Figure 1, the volume of which was known from PV measurements, then lowering the pressure in the system with the mercury leveling bulb. The stopcock was cracked to allow some of the second gas to flow into the system and closed while the pressure was still slightly below 1 atm. After leveling the mercury surfaces the volume of the second gas could be measured and the composition of the hydrogen-deuterium mixture determined. The gases were mixed, and the experimental thermal
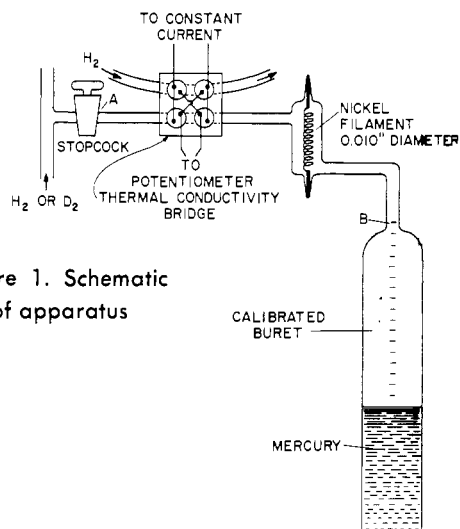

Figure 1. Schematic of apparatus

conductivities of the unequilibrated mixtures calculated by means of Equation 2 are shown in Figure 2 as circled dots. The purity of the deuterium used for making the hydrogen-deuterium mixtures was claimed by the Stewart Oxygen Co. of San Francisco to be greater than 99.5%, the impurity probably being HD. Calculations of the effect of 0.5% HD on the thermal conductivity of hydrogen-deuterium mixtures showed it to be rather small, and for mixtures containing more than 50% hydrogen the error was entirely negligible.

Before equilibrating, a portion of the hydrogen-deuterium mixture was pushed out of the system until all that remained
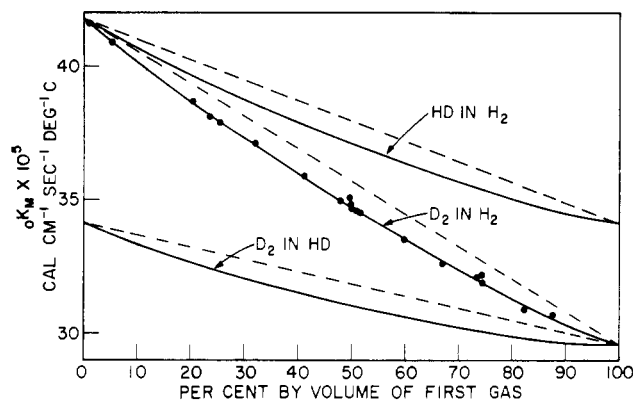
Figure 2. Thermal conductivity of binary mixtures

was the volume included between A and B. The nickel wire was heated electrically to approximately 500° C. for 30 minutes while the leveling bulb was lowered and raised frequently to stir the mixture as much as possible. After allowing the system to cool to room temperature, the bridge output was measured with a potentiometer, and the nickel wire was again heated for 30 minutes. Usually, the bridge output after the second heating was identical with the first measurement, but when any difference between the two measurements was noted, further readings were taken until a constant value was obtained. The experimental thermal conductivities of the equilibrated mixtures were calculated by means of Equation 2; it is these values which are compared with those calculated by the procedure outlined below.

METHOD OF CALCULATION

To compare experimental and calculated values, a triangular graph is used from which the thermal conductivity of any mixture of H_2, D_2, and HD, whether completely equilibrated or not, could be estimated with reasonable accuracy (Figure 3). With a pure gas at each corner of the triangle, such a graph could be used for determining the termal conductivity of a ternary mixture only when it was known accurately how thermal conductivity varied with composition for each of the three binary mixtures represented by the three sides of the triangle. Before calculating the thermal conductivity of these three binary mixtures, values for the thermal conductivities of H_2, HD, and D_2 must be adopted. The value chosen for the thermal conductivity of hydrogen at 0° C. is 41.8×10^{-5} cal. cm.$^{-1}$sec.$^{-1}$deg.$^{-1}$C., the average of the data referred to by Van Cleave and Maas (8). Assuming that the conductivities of
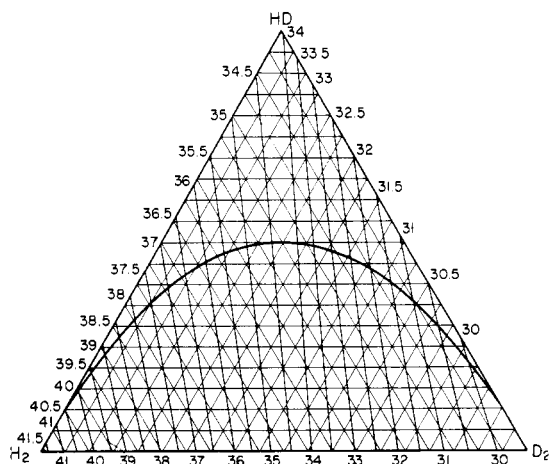

Figure 3. Thermal conductivity-composition relationships

Curved line: Equilibrium isotherm, H_2 – D_2 – HD system, (E = 4) in mole per cent

Straight vertical lines: Lines of constant thermal conductivity, $_0K_M \times 10^5$ cal.$^{-1}$ cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$ C.

HD and deuterium bear the same relation to that of hydrogen as the square root of the inverse ratio of their masses,

$$_0K_H/_0K_{HD} = (3/2)^{1.2} \text{ and } _0K_H/_0K_D = (2)^{1.2} \tag{3}$$

This procedure is justified by the results of Van Cleave and Maas (7) who found from viscosity measurements that the molecular diameter and the mean free path of deuterium is the same as for hydrogen and presumably these properties would be the same for HD as for the other two gases. From Equation 3 it is found that the thermal conductivity at 0° C. of $HD(_0K_{HD})$ is 34.12×10^{-5}, and that of $D_2(_0K_D)$ is 29.56×10^{-5}. Using these figures for the thermal conductivities of the three gases the following ratios result:

$$_0K_H/_0K_{HD} = 1.225, \quad _0K_{HD}/_0K_D = 1.155 \text{ and}$$

$$_0K_H/_0K_D = 1.414 \tag{4}$$

The only binary mixtures studied experimentally were those of hydrogen and deuterium; hence, it appeared to be necessary to obtain an accurate relation between observed thermal conductivities of the hydrogen-deuterium mixtures and their composition. Such an expression for the hydrogen-deuterium mixtures could then be used with confidence for the HD-H_2 and D_2-HD mixtures which could not be studied experimentally. Employing a phenomenological approach, a simple expression has been found for the thermal conductivity of a binary mixture involving only the thermal conductivities of the pure gases and the mole fractions of each constituent.

Derivation of Equation for Binary Mixtures. The simple rule of mixtures for the thermal conductivity of a binary mixture as expressed by the relation $K_M = {}_1K_1x + {}_2K_1(1 - x)$ fails because the thermal conductivities of the components are not constant, but vary with the composition of the mixture. A general expression for the thermal conductivity of binary mixtures could be written as

$$K_M = ({}_1K_x)x + ({}_2K_{(1-x)})(1 - x) \tag{5}$$

in which ${}_1K_x + {}_2K_{(1-x)}$ are thermal conductivities of the components at their concentrations in the mixture.

The thermal conductivity of a pure gas does not vary appreciably as the pressure is decreased below atmospheric until rather low pressures are reached. However, the authors assume that when two gases at atmospheric pressure are mixed their thermal conductivities are lower than in the pure state because each gas dilutes the other to an extent depending on their relative concentrations in the mixture.

Let ${}_1K_1$ = thermal conductivity of gas 1 at 1 atm. and let ${}_1K_x$ = thermal conductivity of gas 1 at partial pressure x.

Assuming that in a binary mixture with gas 2, the per cent changes in thermal conductivity of gas 1 is directly proportional to the per cent changes in concentration, which in the limit becomes

$$\frac{d({}_1K_x)}{{}_1K_x} = N_1 \frac{dx}{x} \tag{6}$$

in which N_1 is a constant of proportionality. The solution of Equation 6 is

$$\ln ({}_1K_x) = N_1 \ln x + C \tag{7}$$

When $x = 1$, ${}_1K_x = {}_1K_1$ and $C = \ln {}_1K_1$. Substituting in Equation 7 and reducing,

$${}_1K_x = {}_1K_1 x^{N_1} \tag{8}$$

An expression similar to Equation 8 can be obtained for gas 2, and for the two gases,

$${}_1K_x = {}_1K_1 x^{N_1} \tag{9}$$

$${}_2K_{(1-x)} = {}_2K_1(1 - x)^{N_2}$$

Substituting Equations 9 in 5, for the thermal conductivity of binary mixtures,

$$K_M = {}_1K_1 x^{(1+N_1)} + {}_2K_1(1 - x)^{(1+N_2)} \qquad (10)$$

An alternate form of Equation 10 can be obtained by expanding x^N into a logarithmic series, and neglecting terms higher than the first power,

$$K_M = {}_1K_1(1 + N_1 \ln x)x +$$
$${}_2K_1[1 + N_2 \ln (1 - x)](1 - x) \qquad (11)$$

Although Equation 10 has been adopted in this discussion calculations showed that there is a negligible difference between results obtained with Equations 10 and 11.

In Figure 2, a graph drawn through experimental points for the hydrogen-deuterium mixtures enabled values of the constants N_1 and N_2 to be calculated. The final numerical expression for the hydrogen-deuterium graph is

$$_HK_D \times 10^5 = 41.8x^{1.0338} + 29.56(1 - x)^{1.0478} \qquad (12)$$

In Equation 12 the ratio of the empirical constants $0.0478/0.0338 = 1.4142$ has the same value as the ratio of the thermal conductivities of hydrogen and deuterium—namely, $41.8/29.56 = 1.414$. We have then the empirical relation for hydrogen-deuterium mixtures that

$$N_D/N_H = K_H/K_D \qquad (13)$$

Assuming that the empirical values of N_H and N_D given above can be used in the equations for calculating the thermal conductivities of the hypothetical pairs HD-H_2 and HD-D_2, there remains only the calculation of the constant N_{HD}, because

it cannot be determined experimentally. Using a relation similar to (13) it is found that

$$N_{HD} = N_H K_H/K_{HD} = N_D K_D/K_{HD} \qquad (14)$$

Substituting the values of the conductivity ratios from Equation 4 and the empirical values of constants N_H and N_D in 14 we find $N_{HD} = 0.0414$. The equations finally adopted for calculating the thermal conductivity of the two hypothetical pairs are, for the H_2-HD mixtures,

$$_HK_{HD} \times 10^5 = 41.8x^{1.0338} + 34.12(1 - x)^{1.0414} \qquad (15)$$

For the HD-D_2 mixtures

$$_{HD}K_D \times 10^5 = 34.12x^{1.0414} + 29.56(1 - x)^{1.0478} \qquad (16)$$

With a pure gas at each corner of the triangle in Figure 3, the thermal conductivities (Table I) of the three binary mixtures calculated according to Equations 12, 15, and 16 can be plotted along the three sides of the triangle.

Since the three graphs in Figure 2 do not overlap, it is possible to find mixtures of equal thermal conductivity for the HD-H_2 graph and the upper portion of the hydrogen-deuterium graph while the lower portion of this graph will contain mixtures having the same thermal conductivity as mixtures of D_2 and HD. These points on the sides of the triangle having the same thermal conductivity can be joined as shown in Figure 3, and the thermal conductivity of all mixtures of H_2, D_2, and HD can be estimated from the graph.

It is also possible to calculate the thermal conductivity of any ternary mixture of the isotopes without having to use the triangular graph of Figure 3. Regarding the ternary mixture H_2, HD, and D_2 as composed of the three binary mixtures H_2-HD,

Table I. Thermal Conductivities of Three Binary Mixtures of System H_2 - HD - D_2

				$_0K_M \times 10^5$ Cal. Cm.$^{-1}$ Sec.$^{-1}$ Deg.$^{-1}$ C.		
x or $1 - x$	$x^{1.0338}$	$x^{1.0414}$	$x^{1.0478}$	D_2 in H_2	HD in H_2	D_2 in H_2
0	0	0	0	41.8	41.8	34.12
0.10	0.0925	0.0909	0.0895	40.12	40.58	33.21
0.20	0.1894	0.1871	0.1851	38.66	39.56	32.55
0.30	0.2881	0.2855	0.2830	37.36	38.71	31.92
0.40	0.3878	0.3850	0.3829	36.00	37.78	31.39
0.50	0.4885	0.4859	0.4836	34.71	36.99	30.86
0.60	0.5897	0.5874	0.5855	33.57	36.25	30.49
0.70	0.6932	0.6897	0.6881	32.38	35.57	30.08
0.80	0.7940	0.7936	0.7915	31.30	34.98	29.77
0.90	0.8968	0.8961	0.8954	30.34	34.44	29.57
1.00	1.000	1.000	1.000	29.56	34.12	29.56

Table II. Comparison of Experimental Values of Thermal Conductivity with Calculated Values (Using Figure 3)

Volume % of H_2-D_2		Cal.Cm.$^{-1}$Sec.$^{-1}$ Deg.$^{-1}$ C.	Volume % of Equilibrated H_2-D_2-HD Calcd. for $E = 4.00$			$_0K_M \times 10^5$, Cal.Cm.$^{-1}$Sec.$^{-1}$Deg.$^{-1}$C.		
H_2	D_2		H_2	D_2	HD	Exptl.	Calcd. (graph)	Error, %
12.63	87.37	30.18	1.59	76.33	22.07	30.01	30.04	-0.10
18.02	81.98	30.84	3.54	65.85	30.57	30.68	30.58	0.33
33.18	66.82	32.58	11.01	44.64	44.34	32.32	32.18	0.43
40.30	59.70	33.49	16.24	35.63	48.12	33.20	33.05	0.45
48.61	51.39	34.53	23.63	26.41	49.95	34.25	34.15	0.29
49.20	50.80	34.62	24.20	25.80	49.99	34.41	34.22	0.55
49.90	50.10	34.69	24.90	25.09	50.00	34.40	34.27	0.38
50.33	49.67	34.73	25.33	24.67	50.00	34.42	34.33	0.26
50.33	49.67	34.73	25.33	24.67	50.00	34.42	34.33	0.26
50.33	49.67	34.73	25.33	24.67	50.00	34.40	34.33	0.20
52.11	47.89	34.97	27.27	22.82	49.90	34.62	34.50	0.35
58.94	41.06	35.87	34.75	16.85	48.39	35.61	35.19	1.19
67.81	32.19	37.06	46.00	10.34	43.65	36.77	36.27	1.38
94.70	5.30	40.91	89.69	0.28	10.03	40.83	40.50	0.81
99.01	0.99	41.58	98.02	0.01	1.96	41.57	41.55	0.04

H_2-D_2, and HD-D_2 the thermal conductivity of any mixture of the three gases can be calculated by means of the numerical relations below in which the chemical symbols represent the mole fraction of each gas in the mixture.

$$K_M \times 10^5 = \left[41.8\left(\frac{H_2}{H_2 + HD}\right)^{1.0338} + \right.$$
$$34.12\left(\frac{HD}{H_2 + HD}\right)^{1.0414}\left]\left(\frac{H_2 + HD}{2}\right) + \right.$$
$$\left[41.8\left(\frac{H_2}{H_2 + D_2}\right)^{1.0338} + \right.$$
$$29.56\left(\frac{D_2}{H_2 + D_2}\right)^{1.0478}\left]\left(\frac{H_2 + D_2}{2}\right) + \right.$$
$$\left[34.12\left(\frac{HD}{HD + D_2}\right)^{1.0414} + \right.$$
$$29.56\left(\frac{D_2}{HD + D_2}\right)^{1.0478}\left]\left(\frac{HD + D_2}{2}\right) \quad (17)$$

APPLICATION TO EQUILIBRATED MIXTURES

If 4.00 is taken as the value of the equilibrium constant in Equation 1 the composition of the equilibrated mixture result-

ing from a binary mixture containing 1 mole of hydrogen and x moles of deuterium is given by the relations

Gas	Moles	Mole fraction	
HD	$2x/(1 + x)$	$2x/(1 + x)^2$	
H_2	$1/(1 + x)$	$1/(1 + x)^2$	(18)
D_2	$x^2/(1 + x)$	$x^2/(1 + x)^2$	

Table II contains the composition of the hydrogen-deuterium mixtures and their observed thermal conductivities as plotted in Figure 2. Table II also contains the composition of the ternary mixtures as calculated by the Relations 18. Finally the experimental thermal conductivities of the equilibrated mixtures are compared with those calculated from the curve for $E = 4.00$ in Figure 3.

LITERATURE CITED

(1) Archer, C. T., Proc. Roy. Soc. (London) A165, 478 (1938).
(2) Bolland, J. L. Melville, H. W., Trans. Faraday Soc. 33, 1316 (1937).
(3) Buddenberg, J. W., Wilke, C. R., Ind. Eng. Chem. 41, 1345 (1949).
(4) Farkas, A., Farkas, L., Proc. Roy. Soc. (London) A144, 467 (1934).
(5) Ibbs, T. L., Hirst, A. A., Ibid., A123, 134 (1929).
(6) Lindsay, A. L., Bromley, L. A., Ind. Eng. Chem. 42, 1508 (1950).
(7) Van Cleave, A. B., Maas, O., Can. J. Research 12, 57 (1935).
(8) Ibid., p. 372.
(9) Wassiljewa A., Physik Z. 7, 235 (1904).

Effect of Molecular Structure on Burning Velocity

G. J. GIBBS and H. F. CALCOTE[1]
Experiment Inc., Richmond 2, Va.

The burning velocities of various compounds have been investigated by many observers in an attempt to understand the mechanism of flame propagation. These data have been obtained by four general methods: the propagation of flame in a tube, in a spherical bomb, in a soap bubble, and on a Bunsen burner (3, 4, 8, 12, 16, 17, 22, 23, 30, 36). Such data on many fuel types are important in verifying theories of flame propagation and ignition and the data reported herein have already been so employed (11, 24, 32). By altering the fuel structure (6), the data are made available for examining such considerations and for predicting the burning velocity of most new systems. Combustibles for which good burning-velocity data are already available have also been studied, to demonstrate the degree to which such data, taken in different laboratories and by different methods, can be compared.

To carry out this program successfully, it is necessary to have a simple yet reliable method of calculating the burning velocity from the flame dimensions. Although there are a number of methods for determining burning velocities from Bunsen burner flame cones, those which have a reasonable theoretical basis and give reliable results require somewhat detailed measurements or calculations (14, 15, 19, 31, 33, 34). This report presents a simple procedure which requires a minimum of calculations to obtain reliable results with data demonstrating the errors involved, a comparison with results from other laboratories, and the burning velocities of 77 compounds showing the effect of molecular structure on burning velocity.

APPARATUS AND PROCEDURE

The apparatus is basically the same as that used by other investigators. Provision is made for controlling and measuring flow rates of air, gaseous fuels, and liquid fuels. The liquid fuels

[1] Present address, AeroChem Research Laboratories, Inc., P. O. Box 12, Princeton, N. J.

are vaporized and fed to the burner in the gaseous form (5). Air is taken from the laboratory supply and metered with a sonic-orifice flowmeter. Gaseous fuels are taken directly from tanks and the pressure is controlled with a Moore Products Nullmatic pressure regulator; the flow rate is determined with a sonic-orifice flowmeter calibrated for each gas. A mixing chamber containing two porous stainless steel disks and filled with glass Raschig rings both aids mixing and prevents flash-back through the gas-feed tubes. All tubing and valves with which the gas comes in contact beyond the liquid-fuel-injection system are Type 316 stainless steel. The burners are seamless stainless steel tubing which can be easily exchanged at a flange on the mixing chamber. Both the air meter and gaseous fuel meter are calibrated by a water-displacement method.

The flame is photographed with a Speed Graphic camera having an f 4.7 lens using Ansco SSS-Ortho film, varying exposure times from 1/25 to 1/100 second. Shadowgraphs of the flame are made by photographing the shadow formed by the heated gases in the inner cone refracting the light from a 2-watt Western Union concentrated arc lamp serving as a point of light source. A Speed Graphic camera without a lens is used, and the exposure time (1/15 to 1/25 second) is controlled by a focal-plane shutter. The burner is placed between the lamp and the film, 61 cm. from the lamp and normally 30 cm. from the film. A scale is photographed on each picture for determining the magnification factor, M.

The methodology involved in calculating burning velocities from the photographs or tracings was derived by considering the volume rate of flow through a section of the flame surface over which the burning velocity is essentially constant. This condition is satisfied if the tip and base of the flame are neglected. Then, the burning velocity is equal to the volume rate of gas flow through a lateral area of the frustum of flame surface divided by that lateral area. The volume rate of gas flow