Gaseous Thermal Conductivity of Hydrogen Chloride, Hydrogen Bromide, Boron Trichloride, and Boron Trifluoride in the Temperature Range from 55 to 380 °C

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Thermal conductivity values of gaseous hydrogen chloride, hydrogen bromide, boron trichloride, and boron trifluoride have been experimentally determined at one atmospheric pressure and in the temperature range from 55 to 380 °C using a differential hot-wire method. Thermal conductivity values of argon were also measured for the purpose of checking the accuracy of the instrumentation. The experimental values are compared with the available literature results. The reproducibility of the results was within 4% over the temperature range.

Introduction

Accurate values of thermal conductivity of halogenated gases such as hydrogen chloride (HCl), hydrogen bromide (HBr), boron trichloride (BCl_3), and boron trifluoride (BF_3) are required for engineering design purposes. A search of the literature indicated a few measurements of thermal conductivity for gaseous hydrogen halides and boron trihalides using different techniques (*1–8*). The present paper reports experimental thermal conductivity values of hydrogen chloride, hydrogen bromide, boron trichloride, and boron trifluoride in the temperature range from 55 to 380 °C at 1 atm using a differential hot-wire technique. The results are compared with the available literature data.

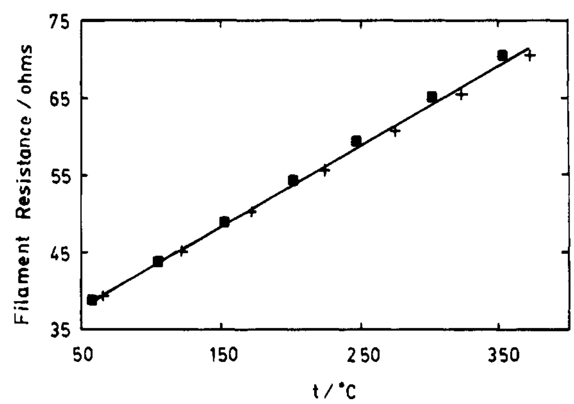

Figure 1. Filament resistance versus temperature for two different sets of data: (■) set 1; (+) set 2.

Experimental Section

Materials. Highly pure samples of argon (99.99 mol %), hydrogen chloride (99.0 mol %), hydrogen bromide (99.8 mol %), boron trichloride (99.9 mol %), and boron trifluoride (99.5 mol %) as obtained from Matheson Gas Products were used without further purification. These gases are highly toxic, and their contact with the skin or direct inhalation should be avoided. Necessary precautions were taken in the handling of these chemicals.

Measurements. The hot-wire thermal conductivity apparatus described earlier in some detail in the literature (*3, 4*) has been used in this work. The thermal conductivity cell or catharometer used is the thermal conductivity detector of a Tracor 560 series gas chromatograph. The circuit response was monitored by a Soltec recorder, Model BC 82000.

The hot-wire cell consists of two identical pairs of matched tungsten–rhenium filaments mounted in cavities in a stainless steel block into which gases can be introduced. The filaments are connected as elements of a constant current Wheatstone bridge. The cell is heated electrically, and the temperature is controlled by a digital temperature controller to within ±0.1 °C. The temperature is measured by calibrated thermocouples mounted on the cell.

The cell consists of two parts, one for the reference gas and other for the sample gas. The thermal conductivity values were determined from the response of the cell with a reference gas of known thermal conductivity in the reference side of the cell and the gas whose thermal conductivity is to be measured in the sample side of the cell. The cell constant, b, is calculated as (*3, 4*)

$$E - E_{ref} = b(1/k - 1/k_{ref}) \tag{1}$$

where E is the unbalanced voltage with the sample gas on one side and the reference gas on the other side of the thermal conductivity cell and k and k_{ref} are the thermal conductivity values of the sample gas and the reference gas, respectively. The value of b is determined by using a standard gas of known thermal conductivity and determining its E values with respect to the reference gas. Prepurified helium (99.2 mol %) was used as the reference gas for all measurements, and prepurified nitrogen (99.7 mol %) was used as the standard gas to find the value of b. The cell constant is sensitive to temperature and, hence, it is determined at all experimental temperatures.

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Table 1. Comparison of Gaseous Thermal Conductivity, λ, of Argon at Different Temperatures

present work							
set 1		set 2		ref 10		ref 8	
t/°C	λ/(mW·cm⁻¹·K⁻¹)	t/°C	λ/(mW·cm⁻¹·K⁻¹)	t/°C	λ/(mW·cm⁻¹·K⁻¹)	t/°C	λ/(mW·cm⁻¹·K⁻¹)
58.7	0.1982	73.5	0.2050	60	0.185	67	0.197
104.5	0.2192	128.4	0.2307	100	0.204	107	0.215
154.3	0.2410	177.5	0.2535	150	0.213	147	0.233
204.1	0.2617	229.4	0.2743	200	0.236	215	0.258
252.3	0.2825	277.4	0.2909	250	0.256	277	0.285
306.3	0.2996	325.1	0.3099	300	0.296	327	0.322
357.9	0.3193	372.5	0.3266	350	0.314	427	0.339

Table 2. Experimental Thermal Conductivity, λ, of Gaseous Halides at Different Temperatures

t/°C	λ(HCl)/(mW·cm⁻¹·K⁻¹)	t/°C	λ(HBr)/(mW·cm⁻¹·K⁻¹)	t/°C	λ(BCl_3)/(mW·cm⁻¹·K⁻¹)	t/°C	λ(BF_3)/(mW·cm⁻¹·K⁻¹)
61.0	0.1669	68.1	0.1053	77.0	0.1293	73.1	0.2186
106.4	0.1880	113.2	0.1213	134.6	0.1524	125.5	0.2482
155.7	0.2104	161.5	0.1398	180.6	0.1698	172.4	0.2768
204.9	0.2335	210.7	0.1590	232.3	0.1888	224.3	0.3070
252.5	0.2575	258.5	0.1789	284.1	0.2074	276.8	0.3396
307.3	0.2813	311.5	0.1972	330.7	0.2239	324.7	0.3705
359.0	0.3069	360.0	0.2157	380.5	0.2414	372.3	0.3996

During the measurement of thermal conductivity, it was noticed that the gas may not be at a uniform temperature due to the temperature difference between the cell wall and the filament wire. This temperature difference is minimized by operating the apparatus at a sufficiently low filament current. This required a means of monitoring the temperature of the filament wire and was accomplished by using the filament as a resistance thermometer. The filament resistance was calculated by monitoring the current through the filament, and the potential across the filament was calculated by the product of filament current (in amperes) and filament resistance (in ohms).

The temperature corresponding to a particular filament resistance was obtained from a knowledge of the temperature coefficient of resistance. The temperature coefficient of resistance for the filament used in this study was determined, and the results are presented in Figure 1. During data acquisition, the filament current was adjusted such that the difference in the temperature of the cell wall and the filament was kept at a minimum. This minimizes the end effect, the temperature discontinuity, and the interchange energy between the gas molecules and the solid surface. Argon was chosen because its literature values were available in the temperature range of this study for the purpose of comparison and to test the validity of the method used.

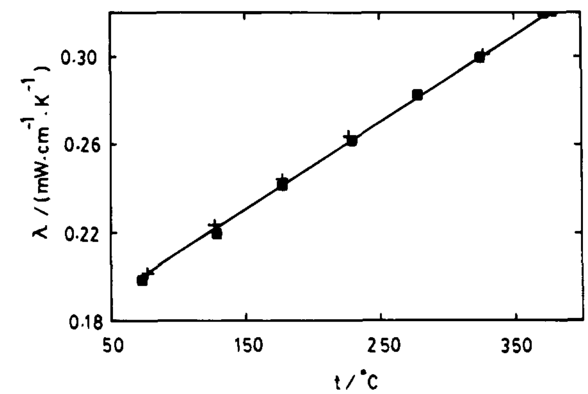

Figure 2. Literature comparison of thermal conductivity values of argon as a function of temperature: (■) present values; (+) ref 7.

Table 3. Least-Squares Fitted Coefficients of Equation 2

gas	a	b·10³	c·10⁶	d·10⁹
Ar (set 1)	0.1694	0.5033	−0.2448	0.0161
Ar (set 2)	0.1635	0.6140	−0.7538	0.7571
HCl	0.1394	0.4453	0.1009	−0.1221
HBr	0.0834	0.2891	0.5021	−0.7976
BCl_3	0.0962	0.4509	−0.2906	0.2855
BF_3	0.1793	0.5171	0.3055	−0.2774

Results and Discussion

Two sets of the experimental data are reported for argon because one pair of filaments was replaced with new filaments during the course of the data collection. However, the average percent error between the two sets of data was within ±0.4%. The experimental λ values of argon are compared in Table 1 with the available literature results. The present values are generally higher when compared to the most recent literature data (*9–11*) in the range of experimental temperatures. A typical deviation of λ values for argon with the literature values (*5*) is shown in Figure 2. Also, the present values are about 2% lower than those of Touloukian et al. (*5*). It may be noted that the literature values were published over a wide range of temperatures and pressures, making it difficult for direct comparison (*8*). However, it is realized that thermal conductivity increases by about 1% or less per atmosphere (*2*). Thermal conductivities of HCl, HBr, BCl_3, and BF_3 are given Table 2.

The experimentally determined gaseous thermal conductivity values of different gases are fitted to the empirical equation to estimate the correlation coefficients *a*, *b*, *c*, and *d* using

$$\lambda/(\mathrm{mw\cdot cm^{-1}\cdot K^{-1}}) = a + b\,(t/°\mathrm{C}) + c\,(t/°\mathrm{C})^2 + d(t/°\mathrm{C})^3 \quad (2)$$

The least-squares values of the coefficients *a*, *b*, *c*, and *d* are given in Table 3. The variance is within 10^{-7} in all cases.

The experimental thermal conductivity values as a function of temperature for hydrogen chloride, hydrogen bromide, boron trichloride, and boron trifluoride are presented in Figure 3. The thermal conductivity values for BF_3 are higher than those for BCl_3. On the other hand, HCl exhibits higher thermal conductivity than HBr over the investigated range of temperature. A comparison for HCl is made in Figure 4 between the present values and the published results (*4, 12*). The average deviation is around 1.4% compared with the values of Baker and Brokaw (*4*). However, a comparison to the values of Barua et al. (*12*) shows a standard deviation of 2.4%.

Thermal conductivity values as a function of temperature for gaseous HBr are compared in Figure 5 with the results

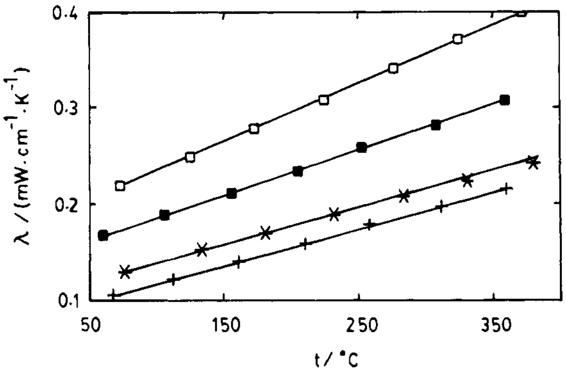

Figure 3. Thermal conductivity versus temperature for (□) BF_3, (■) HCl, (*) BCl_3, and (+) HBr.

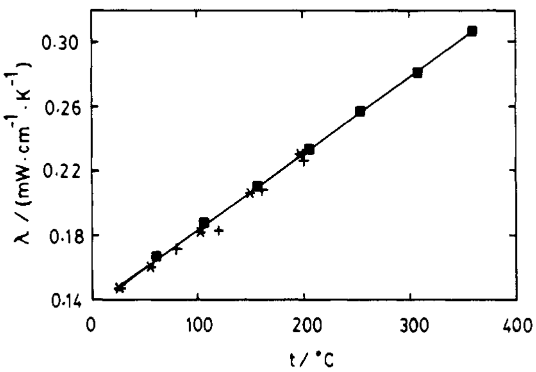

Figure 4. Literature comparison of thermal conductivity values of HCl as a function of temperature: (■) present values; (+) ref 8; (*) ref 6.

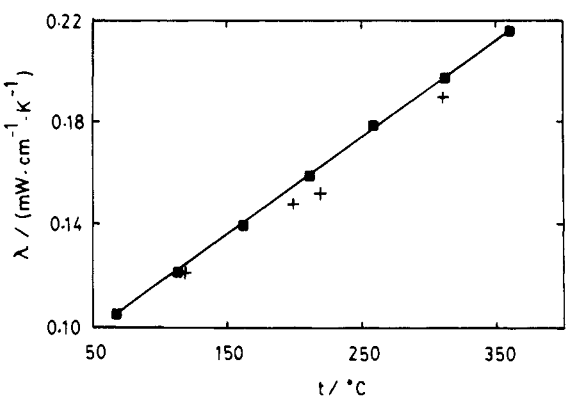

Figure 5. Literature comparison of thermal conductivity values of HBr as a function of temperature: (■) present values; (+) ref 9.

of Franck (*13*), the difference being about 7%. Such a large error may be attributed to the fact that Franck made measurements at 0.5 bar. However, the standard deviation between the correlated values of Yaws (*14*) and the present values is around 5% (not shown graphically).

The experimental gas phase thermal conductivity results for BCl_3 and BF_3 are compared in Figure 6 with the extrapolated values of MacKenzie and Raw (*15*). The latter reported the experimental gaseous thermal conductivity values of boron trichloride and boron trifluoride in the temperature range 0−80 °C. A comparison with their values was made possible by extrapolating the present values close to 0 °C. The average differences between the

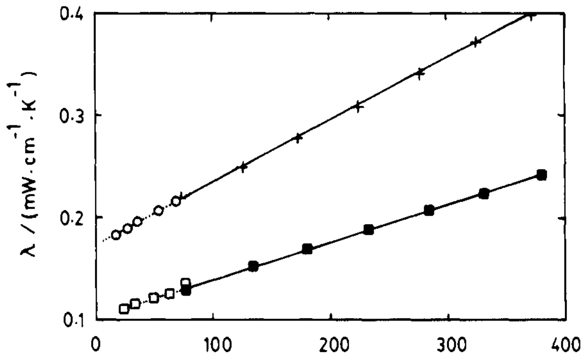

Figure 6. Literature comparison of thermal conductivity values of BCl_3 and BF_3 as a function of temperature: (+) BF_3, present values; (○) ref 11; (■) BCl_3, present values, (□) ref 11.

present values and those of the literature were 0.9 and 4.0%, respectively, for BF_3 and BCl_3. However, the recently published results (*9*) for BF_3 at 1 bar in the temperature range 47−327 °C are about 3−4% lower than the present values.

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Literature Cited

(1) Owens, E. J.; Thados, G. *AIChE J.* **1957**, *3*, 455; **1960**, *6*, 676.
(2) Reid, R. C.; Prausnitz, J. M.; Poling, B. *The Properties of Gases and Liquids*, 4th ed.; McGraw Hill: New York, 1987.
(3) Baker, C. E.; Brokaw, R. S. *J. Chem. Phys.* **1964**, *40*, 1523.
(4) Baker, C. E.; Brokaw, R. S. *J. Chem. Phys.* **1965**, *43*, 3519.
(5) Touloukian, Y. S.; Liley, P. E.; Saxena, S. C. *Thermophysical Properties of Matter, TPRC Data Series, Vol. 3, Thermal Conductivity of Nonmetallic Liquids and Gases*; Plenum: New York, 1970.
(6) Aziz, R. A. *Int. J. Thermophys.* **1987**, *8*, 193.
(7) Younglove, B. A.; Henley, H. J. M. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1323.
(8) Vargaftik, N. B.; Filippov, L. P.; Tarzimanov, A. A.; Totskii, E. E. *Handbook of Thermal Conductivity of Liquids and Gases*; CRC Press: Boca Raton, FL, 1994.
(9) Aziz, R. A.; Chen, H. H. *J. Chem. Phys.* **1977**, *7*, 5719.
(10) Kestin, J.; Knierim, K.; Mason, E. A.; Najafi, B.; Ro, S. T.; Waldman, M. *J. Phys. Chem. Ref. Data* **1984**, *13*, 229.
(11) Vidal, D.; Tufeu, R.; Carrabos, Y. *High Pressure Science and Technology*; Pergamon Press: Oxford, U.K., 1980; pp 692−701.
(12) Barua, A. K.; Manna, A.; Mukhopadhyay, P. *J. Chem. Phys.* **1968**, *49*, 2422.
(13) Franck, E. U. *Z. Electrochem.* **1951**, *55*, 636.
(14) Yaws, C. L. *Physical Properties*, 2nd ed.; McGraw Hill: New York, 1977.
(15) MacKenzie, H. A.; Raw, C. I. G. *J. S. Afr. Chem. Inst.* **1953**, *6*, 8.

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