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## Abstract

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# THERMAL CONDUCTIVITY AND VISCOSITY OF VAPORS OF ZIRCONIUM AND HAFNIUM TETRACHLORIDES IN THE TEMPERATURE RANGE 300–700°

For the development of new methods for separating zirconium and hafnium tetrachlorides, it is necessary to know the constants characterizing molecular transport processes, such as vapor viscosity, its thermal conductivity, heat content, etc. We have determined the thermal conductivity and viscosity of vapors of zirconium and hafnium tetrachlorides in the temperature range 300–700°.

**1. Determination of the thermal conductivity of vapors of $ZrCl_4$ and $HfCl_4$.** The thermal conductivity of the vapors was determined by the "hot-wire" method: in an atmosphere of the given gas, a thin wire is heated by an electric current, the resistance of which, at constant current power, depends on its temperature and, consequently, on the thermal conductivity of the gas.

Measurements were carried out using a special apparatus (Fig. 1) consisting of a double furnace with Duralumin blocks. The temperature of the blocks is measured by means of an EPP-09 electronic automatic potentiometer with a platinum-rhodium thermocouple and is regulated with an accuracy of $±$1° C. A glass cell for measuring thermal conductivity is placed in this furnace. It is a tube made of Pyrex glass, 5-7 mm in diameter, along the axis of which a platinum wire 0.05 mm in diameter is stretched. A platinum electrode is sealed into the top of the tube, to which the central wire is welded. A platinum resistance thermometer is wound bifilarly on the tube to determine the temperature of the tube walls. The lower part of the tube is fused to a wider tube 12-15 mm in diameter. In it there is a centering weight and a current-conducting spring. A platinum electrode is sealed into the lower part of this tube, and a side outlet for filling the cell with the gas under investigation is attached. The temperature of the platinum wire is determined from its resistance; for this purpose a bridge circuit is used. In addition, the resistance of the filament is also calculated by Ohm' s law.

*Fig. 1. Schematic diagram of the apparatus for determining the thermal conductivity of vapors of zirconium and hafnium tetrachlorides. 1, 2 —Duralumin blocks, 3 —cell, 4 —cell outlet with ground joint, 5 —resistance thermometer, 6*

*—weight with centering devices, 7 —spring of platinum wires, 8 —electrode*

During the experiment, the resistance of the platinum filament and of the resistance thermometer is measured at room temperature, and the corresponding plots of their resistances versus temperature are constructed. The cell is then placed in the furnace, and measurements are made of the dependence of the temperature difference between the platinum wire and the tube walls on the power of the current heating the wire, at different wall temperatures in vacuum ($10^{-3}$ mm Hg) and in dry hydrogen. After this, the cell is filled with powder of zirconium or hafnium tetrachloride, evacuated to a pressure of $10^{-3}$ mm Hg, sealed, and again placed in the furnace. The temperature of the lower block is brought to 300-320°. The vapor pressure of the tetrachloride at this

at a temperature approximately equal to 0.75 atm, and the thermal conductivity of the vapor does not depend on pressure. The temperature of the upper block is varied from 350 to 500°. The measurements are carried out as follows: at a given temperature of the ampoule walls, the temperature of the central filament is varied and the consumed electric power is measured. Determinations are carried out within the range of wall temperatures from 350 to 500°. From the measurement results, plots are constructed of the dependence of $W$ on $\Delta T$ at specified temperatures of the ampoule walls and the dependence of $W$ on the wall temperature at constant $\Delta T = 20°$. The thermal conductivity of the tetrachloride vapor is calculated by the formula [1,2]

$$\lambda = \frac{\lambda_1 (W_2 - W_0)}{W_1 - W_0},$$

where $\lambda_1$ is the thermal conductivity of hydrogen at the given temperature; $W_0, W_1, W_2$ are the powers expended to obtain a temperature difference of 20° in vacuum, in hydrogen, and in tetrachloride vapor, respectively.

**Table 1**

Dependence of the thermal-conductivity coefficient of $ZrCl_4$ and $HfCl_4$ vapors on temperature

| Temp., °C | $\lambda \cdot 10^5$, cal/cm · sec · deg | $\lambda \cdot 10^5$, cal/cm · sec · deg |
|---:|---:|---:|
| Temp., °C | $ZrCl_4$ | $HfCl_4$ |
| 300 | 4.31 | 3.67 |
| 350 | 4.87 | 3.95 |
| 400 | 5.43 | 4.26 |
| 450 | 5.96 | 4.58 |
| 500 | 6.35 | 4.89 |

**Table 2**

Dependence of the viscosity coefficient of $ZrCl_4$ and $HfCl_4$ vapors on temperature

| Temp., °C | $\eta \cdot 10^7$, poise | $\eta \cdot 10^7$, poise |
|---|---|---|
| Temp., °C | $ZrCl_4$ | $HfCl_4$ |
| 300 | 1970 | 2680 |
| 400 | 2265 | 3060 |
| 500 | 2640 | 3505 |
| 600 | 2970 | 3870 |
| 700 | 3230 | 4150 |

The results obtained are presented in Table 1 and in Fig. 2. The thermal-conductivity coefficients of the vapors of zirconium and hafnium tetrachlorides, as was to be expected, increase with increasing temperature. This dependence is expressed by a straight line. The thermal conductivity of $ZrCl_4$ vapor is greater than that of $HfCl_4$ vapor, and with an increase in temperature from 300 to 500° this difference increases. Thus, at 300° the thermal-conductivity coefficients of $ZrCl_4$ and $HfCl_4$ are, respectively, $4.31 \cdot 10^5$ and $3.67 \cdot 10^5$; at 500° they are $6.35 \cdot 10^5$ and $4.89 \cdot 10^5$ cal/cm • sec • deg.

**Fig. 2.** Dependence of the thermal conductivity of vapors of zirconium and hafnium tetrachlorides on temperature.

**2. Determination of the viscosity of $ZrCl_4$ and $HfCl_4$ vapors.** The viscosity of tetrachloride vapors was determined by the method of vapor effusion through a capillary ([3,4]). The viscosity coefficient was calculated from the Hagen—Poiseuille formula on the basis of the following quantities established experimentally: the vapor pressures at the inlet and outlet of the capillary, the mass of vapor flowing through the capillary in a known time, and the parameters of the capillary.

For the measurements an apparatus was used that is shown in Fig. 3. It consists of a two-section furnace with nickel and duralumin blocks; the temperature of the nickel block is measured and controlled in the temperature interval 350—700° with an accuracy of $\pm 1.5^\circ$ by an EPV-2 electronic automatic potentiometer. The temperature of the duralumin block is measured with a chromel-alumel thermocouple with a PP potentiometer and is controlled by a separate thermoregulation system with an accuracy of $\pm 0.3^\circ$, in the interval 250—350°. Into the furnace is inserted

a quartz ampoule with a capillary sealed to it, filled with freshly sublimed zirconium or hafnium tetrachloride. The ampoule has a special pocket for a thermocouple. The radius of the capillary is determined with an accuracy of $±$0.003 mm by measuring, on a comparator, the length of a mercury column in the capillary and weighing the mercury on an analytical balance.

Fig. 3. Diagram of the setup for determining the viscosity of zirconium and hafnium tetrachloride vapor. 1 —nickel block, 2 —duralumin block, 3 —ceramic ring, 4 —ampoule with capillary, 5 —thermocouple lead

Figure 1: Fig. 3. Diagram of the setup for determining the viscosity of zirconium and hafnium tetrachloride vapor. 1 —nickel block, 2 —duralumin block, 3 —ceramic ring, 4 —ampoule with capillary, 5 —thermocouple lead

The measurements are carried out as follows. The ampoule is filled with powder of freshly sublimed zirconium or hafnium tetrachloride to approximately 1/3 of its volume and the side arm is sealed, after which the ampoule is weighed. A thermocouple is inserted into the pocket of the ampoule, and the entire ampoule is placed in the furnace blocks heated to the specified temperatures, with the capillary placed in the nickel block and the bulb in the duralumin block. In the furnace the ampoule is held for 5-10 min, after which it is removed, cooled, and weighed; in this way the amount of tetrachloride that has passed through the capillary is measured. The vapor pressure of the tetrachloride inside the ampoule is determined from the temperature using equations (5):

**Fig. 3.** Diagram of the setup for determining the viscosity of zirconium and hafnium tetrachloride vapor.
1 —nickel block, 2 —duralumin block, 3 —ceramic ring, 4 —ampoule with capillary, 5 —thermocouple lead.

$$\lg P_{\mathrm{mm}} = -\frac{5400}{T} + 11.766 \text{ for } \mathrm{ZrCl_4} \quad \text{and} \quad \lg P_{\mathrm{mm}} = -\frac{5197}{T} + 11.712 \text{ for } \mathrm{HfCl_4}.$$

In this case the temperature of the duralumin block is selected so that the pressure inside the ampoule is 200 mm Hg. The vapor-viscosity coefficient at the given capillary temperature is calculated by a formula including the correction for gas expansion in the capillary:

$$\eta = \frac{\pi r^4 \tau \rho}{8ML} \cdot \frac{p_1^2 - p_2^2}{2p_1},$$

where $r$ is the radius of the capillary, $p_1$ is the pressure in the ampoule, $p_2$ is atmospheric pressure, $\tau$ is the duration of the experiment, $M$ is the loss of weight of the ampoule, $L$ is the length of the capillary, and $\rho$ is the vapor density in the capillary at the pressure and temperature of the capillary, calculated using the gas laws while assuming the vapor to be an ideal gas; for the given pressure and temperature such an assumption is entirely permissible. The measurements were carried out in the range 350–700°. Their results are presented in Table 2 and in Fig. 4.

**Fig. 4.** Dependence of the viscosity of zirconium and hafnium tetrachloride vapors on temperature.

Fig. 4. Dependence of the viscosity of zirconium and hafnium tetrachloride vapors on temperature

Figure 2: Fig. 4. Dependence of the viscosity of zirconium and hafnium tetrachloride vapors on temperature

The viscosity coefficients in the temperature range studied vary directly proportionally to temperature, and the viscosity of $HfCl_4$ vapor somewhat exceeds the viscosity of $ZrCl_4$ vapor. Thus, for example, at 500°C $\eta_{ZrCl_4} = 2640 \cdot 10^{-7}$ poise, while $\eta_{HfCl_4}$ is $3505 \cdot 10^{-7}$ poise. It should be noted that the viscosity of $HfCl_4$ vapor increases with increasing temperature to a somewhat greater extent than that of $ZrCl_4$.

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*Note: Figure translations are in progress. See original paper for figures.*