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Abstract

Full Text

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CHEMISTRY

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STUDY OF THE VAPOR DENSITY OF HAFNIUM TETRACHLORIDE AT HIGH TEMPERATURES

The literature contains no data on the effect of temperature and pressure on the vapor density of hafnium tetrachloride at constant pressure or temperature, respectively. However, such information is necessary for calculations of certain technological processes for separating zirconium and hafnium tetrachlorides in the gaseous state.

We have studied the vapor density of hafnium tetrachloride under various conditions using a γ-radioactive isotope, by the method described in ([1],[2]).

Fig. 1. Schematic of the apparatus for determining the vapor density of hafnium tetrachloride at high temperatures.
1 —furnace No. 1; 2 —furnace No. 2; 3 —quartz apparatus; 4 —asbestos and aluminum screen; 5 — "housing" with counting tube; 6 —PS-100 counting circuit; 7 —EPP-09 automatic electronic potentiometer; 8 —load resistance; 9 —autotransformer; 10 —voltage stabilizer; 11 —thermocouples; *a* —capillary-winding power supply.

For the measurements, hafnium tetrachloride labeled with the isotope Hf^{181} was used ($T_1/_2$ = 45 days, $\epsilon\beta$ = 0.41 MeV, $\epsilon\gamma$ = 0.133-0.428 MeV). The preparation, with a specific activity of 50 mCi/g, was obtained by chlorinating metallic hafnium irradiated with slow neutrons in a uranium reactor. The tetrachloride thus prepared was purified by twofold sublimation in a stream of hydrogen and

in vacuum. All operations for obtaining and purifying the labeled hafnium tetrachloride were carried out in a hot radiochemical hood. The purified preparation contained 0.3% zirconium tetrachloride and less than 0.001% Fe, Ti, Si, Al.

Figure 1 shows a schematic of the apparatus used. Furnace No. 1 had a massive block of stainless steel, and furnace No. 2 was made of aluminum. The furnaces were arranged at right angles so that radiation from the vessel located in the second furnace would not reach the counter installed opposite the opening of the first furnace. The furnace temperature was measured with chromel-alumel-

···thermocouples connected to automatic electronic potentiometers EPP-09, and was regulated by three-position devices,

Table 1

Dependence of the vapor density of hafnium tetrachloride on temperature at constant pressure

0.5 atm	0.5 atm	0.5 atm	1.0 atm	1.0 atm	1.0 atm	1.5 atm	1.5 atm	1.5 atm
temp., °C	vapor density, g/cm^3 · 10^{-3}	deviation from theory, %	temp., °C	vapor density, g/cm^3 · 10^{-3}	deviation from theory, %	temp., °C	vapor density, g/cm^3 · 10^{-3}	deviation from theory, %
395	2.958	1.6	406	5.925	3.2	391	7.981	10.0
450	2.779	2.8	481	5.305	2.4	476	7.218	8.3
534	2.446	1.2	490	4.830	1.4	518	6.924	6.9
572	2.330	0.9	592	4.700	2.7	570	6.623	4.9
628	2.230	2.7	616	4.510	2.6	657	6.097	3.2
696	2.068	2.6	718	4.030	2.2	671	6.006	3.2
740	1.910	0.8	804	3.700	2.0	745	5.691	1.1
810	1.803	0.0	852	3.535	1.8	804	5.353	1.4
940	1.600	0.6	860	3.510	1.8	840	5.247	0.3
1000	1.507	1.7	952	3.211	0.7	935	4.821	0.5

built into the potentiometers according to a heating-preheating circuit. At the ends of the furnace blocks there were additional heating windings; all the windings were supplied with stabilized current. The accuracy of temperature regulation in the first furnace was $±$1°, and in the second $±0.5°. *Quartz vessels connected to one another by a heated capillary bent at a right angle were placed in the furnace. T* was chosen in such a way that, at different vessel temperatures under conditions of established equilibrium, there was no noticeable pressure difference caused by the superposition of the Knudsen effect. The temperature of the capillary was maintained at 550 ± 10°. The temperature of the vessels was determined by the compensation method using calibrated chromel-alumel thermocouples,

Fig. 2. Dependence of the radiation intensity of the vessel in furnace No. 1 on the temperature of furnace No. 2. 1 —temperature run upward, 2 — temperature run downward

Figure 2: Fig. 2. Dependence of the radiation intensity of the vessel in furnace No. 1 on the temperature of furnace No. 2. 1 —temperature run upward, 2 — temperature run downward

which were placed in special sheaths inside the vessels. The accuracy of temperature measurement was $±$0.5°. Hafnium tetrachloride was loaded into the vessels by sublimation. Before sealing, the apparatus was evacuated to a residual pressure of $2 \cdot 10^{-6}$ mm Hg. The total activity of the loaded amount was ~5 mCu.

Fig. 2. Dependence of the radiation intensity of the vessel in furnace No. 1 on the temperature of furnace No. 2.
1 —temperature run upward, **2** —temperature run downward

We carried out three series of experiments under isothermal and isobaric conditions. In the first case, furnace No. 1 was thermostated, where the higher temperature—400-1000°—was maintained, while the temperature of furnace No. 2 varied from 280 to 350°.

The pressure in the system in the presence of a solid phase was determined by the temperature of the less-heated furnace No. 2, where the vessel with the solid phase was located, and was calculated on the basis of the dependence of the vapor pressure of hafnium tetrachloride on temperature ([3,4]). The moment of disappearance of the solid phase was established···

by the sharp break in the curve expressing the dependence of the radiation intensity of furnace vessel No. 1 on the temperature of furnace No. 2.

Table 2

Dependence of the vapor density of hafnium tetrachloride on pressure at constant temperature

398°	398°	398°	467°	467°	467°	865°	865°	865°
Pressure, mm Hg	Vapor density, g/cm^3 $\cdot 10^{-3}$	Deviation from theory, %	Pressure, mm Hg	Vapor density, g/cm^3 $\cdot 10^{-3}$	Deviation from theory, %	Pressure, mm Hg	Vapor density, g/cm^3 $\cdot 10^{-3}$	Deviation from theory, %
130	1.008	1.3	100	0.676	2.9	130	0.580	1.0
190	1.422	2.2	200	1.361	1.9	200	0.890	1.3
240	1.797	2.3	260	1.781	1.3	290	1.285	2.0
310	2.325	2.1	370	2.478	3.7	500	2.208	2.1
400	2.959	3.4	440	2.968	2.9	750	3.308	2.4

Fig. 3. Dependence of the vapor density of hafnium tetrachloride on temperature at constant pressure. 1 —heating, 2 —cooling

Figure 3: Fig. 3. Dependence of the vapor density of hafnium tetrachloride on temperature at constant pressure. 1 —heating, 2 —cooling

398°	398°	398°	467°	467°	467°	865°	865°	865°
560	4.305	3.1	640	4.356	2.0	870	3.836	2.3
770	5.696	3.5	920	5.526	3.0	950	4.230	1.4
850	6.278	3.6	980	6.492	3.3	1010	4.499	1.6
640	4.777	2.5				1140	5.093	1.0
140	1.083	1.1				1240	5.464	2.4

In carrying out the process isobarically, furnace No. 2 was thermostated; in it a lower temperature was maintained (280-350°), and the temperature of furnace No. 1 was varied from 400 to 1000°.

Radiometric measurements were carried out while raising and lowering the temperature. The measured values agreed well with one another. The radiation intensity was measured at each point 3 times for 100 sec, using an electronic stopwatch interlocked with the counting circuit PS-100. Before the measurements, the required temperature was established in the vessels; it was maintained for 30 min and monitored from the recording on the potentiometers' strip chart. After completion of the measurements, a reference radiation intensity was established. For this purpose, part of the hafnium tetrachloride was distilled into the vessel of furnace No. 1, after which the capillary connecting the vessels was sealed off approximately at the bend, from where the radiation no longer reached the counter. Then, upon heating the vessel and the capillary to 550°, i.e., above the critical temperature of hafnium tetrachloride ([5]), the radiation intensity was measured. After this the cooled vessel was opened and washed free of the condensed hafnium tetrachloride; its amount was determined by the usual weighing method. From the weight of hafnium tetrachloride, the volume of the vessel, and the reference radiation intensity, a conversion coefficient was calculated for converting the number of pulses into density, expressed in g/cm^3. It proved to be equal to $1.8907 \cdot 10^{-5}$.

Fig. 3. Dependence of the vapor density of hafnium tetrachloride on temperature at constant pressure. 1 —heating, 2 —cooling

The results obtained are presented in Tables 1 and 2 and in Figs. 2 and 3. The overall measurement error was $±2.5^{6}$), zirconium tetrachloride vapors under analogous conditions

under such conditions behave in the same way. When the pressure is increased above atmospheric and the temperature is lowered to values close to the sublimation temperature, the behavior of hafnium tetrachloride vapor deviates to

a greater extent from that of an ideal gas; moreover, the divergence toward a decrease in the density of the real vapor reaches 10%. This deviation cannot be explained by phenomena of molecular association and, apparently, it depends on the nonideality of the vapor near the condensation temperature.

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CITED LITERATURE

1. F. S. Dainton, H. M. Kimberley, Trans. Farad. Soc., **46**, 912 (1950).
2. V. V. Illarionov, S. A. Cherepanova, DAN, **133**, 1086 (1960).
3. A. A. Palko, A. D. Ryon, D. W. Kuhn, J. Am. Chem. Soc., **62**, 319 (1958).
4. Sun Ying-chzhu, I. S. Morozov, ZhNKh, **4**, 492 (1959).
5. L. A. Nisel' son, ZhNKh, **6**, 1243 (1961).
6. W. Fisher, Zg. anorg. u. allgem. Chem., **211**, 321 (1933).

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