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Abstract

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STUDY OF THE THERMAL STABILITY OF MOLECULES OF ZIRCONIUM AND HAFNIUM TETRAHALIDES UPON IMPACT WITH A HOT SURFACE IN VACUUM

To solve a number of theoretical questions connected with the processes of separating zirconium and hafnium, it is necessary to know the thermal stability of their tetrahalides, in particular the probability of decomposition of this type of molecule upon a single impact with a hot surface. The literature contains only data on the decomposition coefficient of zirconium tetraiodide as a function of temperature [1,2]. Its molecules decompose completely upon impact with a surface heated to 1300–1500°. We have determined the decomposition coefficients of zirconium and hafnium tetrahalides (with the exception of fluorides) as a function of the temperature of the hot surface.

A commercial preparation of zirconium tetrachloride was used for the study. Hafnium tetrachloride was obtained by chlorinating a mixture of hafnium oxide with sugar charcoal. Zirconium and hafnium tetrabromides were obtained by brominating the metals at a temperature of 600°. Purified and thoroughly dried argon was used as the carrier. The tetraiodides of both elements were synthesized by the interaction of the metals with purified iodine sublimate in vacuum in sealed ampoules. All the tetrahalides used were purified by double sublimation in a stream of hydrogen and in vacuum in order to remove impurities of volatile halides (Fe, Ti, Al, Si) and possible hydrolysis products. In the preparations obtained, the content of metal and halogen was determined gravimetrically in the form of zirconium (hafnium) dioxide and silver halides. The presence of impurities was established by the spectral method. The results of the analyses are given in Table 1. All operations with the tetrahalide were carried out in a dry chamber.

Table 1

Results of analyses of the starting preparations

Figure 1

Figure 1: Figure 1

Substance	Zr, % found	Zr, % calc.	Hf, % found	Hf, % calc.	Halogen, % found	Halogen, % calc.	C, content % Fe	C, content % Ti	C, content % Si	C, content % Al	C, content % Mg
$ZrCl_4$	39.40	39.14	0.10	–	60.46	60.86	0.005	0.011	0.09	0.004	0
$ZrBr_4$	21.78	22.20	0.39	–	76.88	77.80	0.005	0.009	0.21	0.003	0.016
ZrJ_4	15.41	15.23	0.16	–	84.03	84.77	0.004	0.006	0.08	0.003	–
$HfCl_4$	0.38	–	56.28	55.73	43.13	44.27	0.004	0.002	0.12	0.004	0.003
$HfBr_4$	0.24	–	36.33	35.84	63.22	64.16	0.003	0.001	0.13	0.003	0.002
HfJ_4	0.18	–	26.74	26.06	72.03	73.94	0.002	0.001	0.10	0.003	0.002

The diagram of the apparatus used to measure the decomposition coefficients of zirconium and hafnium halides is shown in Fig. 1. The setup consists of a chamber **1** with a branch tube **2**, into which an ampoule containing the tetrahalide under investigation is inserted. In the upper part of the ampoule there is a capillary opening through which vapors of the tetrahalide flow out until equilibrium conditions are established. The branch tube is heated by a special removable heater **3**. The walls of the chamber that bound the space above the ampoule are cooled with liquid nitrogen to condense the undecomposed tetrahalide and the liberated halogen. Above the capillary opening of the ampoule there is a target **4** made of molybdenum foil 0.5 mm thick and

12–15 mm wide. It is heated to the required temperature by an electric current supplied through molybdenum leads 5. The temperature of the target is measured through viewing window 6 with optical pyrometer 8. The entire system is connected to the vacuum line through spherical trap 7, cooled with liquid nitrogen 9. Before the experiment begins, a weighed ampoule containing the tetrahalide under investigation is lowered into the instrument, and the instrument is evacuated to a residual pressure of the order of 10^{-6} mm Hg, which is maintained throughout the experiment. The target is heated to the specified temperature, and a heater is brought up over the side arm; the temperature of this heater is determined by the vapor pressure of the given tetrahalide required for the experiment. Heating is continued until approximately 0.3 g of tetrahalide has been removed from the ampoule (15–20 min). After this the heater is lowered, and after 10 min the incandescence of the target is stopped.

Fig. 1. Diagram of the apparatus for determining the decomposition coefficients of zirconium and hafnium tetrahalides on a heated surface.
1 –instrument, 2 –side arm for holding the ampoule, 3 –heater, 4 –molybdenum target, 5 –molybdenum electrical leads, 6 –viewing window, 7 –trap, 8 –pyrometer, 9 –liquid nitrogen

Figure 2

Figure 2: Figure 2

When the molecules of tetrahalides strike the hot surface, they decompose partially or completely according to the scheme:

$$\mathrm{Me}\Gamma_4 = \mathrm{Me} + 2\Gamma_2.$$

The formation of lower halides under the experimental conditions was excluded, since above 600° they disproportionate completely into the metal and halogen.

Fig. 2. Dependence of the decomposition coefficients of zirconium and hafnium tetrahalides on the surface temperature.
1 –ZrJ_4, 2 –HfJ_4, 3 –$ZrBr_4$, 4 –$HfBr_4$, 5 –$ZrCl_4$

During the experiment, metallic zirconium or hafnium is deposited on the target in the form of a shiny, tightly adhering coating. After the experiment is completed, the ampoule is weighed, and the amount of metal released as a result of dissociation of the tetrahalide is determined chemically. For this purpose the molybdenum target is dissolved in nitric acid, which does not react at all with the zirconium or hafnium deposited on it. They separate in the form of a plastic foil shaped like a disk 8-10 mm in diameter and are weighed. According to spectral-analysis data, this foil contains only an insignificant amount of molybdenum, which penetrated into it, probably as a result of diffusion from the target material.

In order to calculate the decomposition coefficient from the experimental data, it is necessary to know what number of molecules of the tetrahalide evaporating from the ampoule actually strikes the target. For this purpose, a definite pressure is produced in the ampoule; it must be kept constant by selecting the appropriate heater temperature, since the dependence of the vapor pressure of zirconium and hafnium tetrahalides on temperature is known ([3–7]), and it may be assumed that the capillary opening in the ampoule offers a significant resistance to the molecular flow. The pressure was maintained at such a level that the mean free path of the molecule was, by order of magnitude, considerably greater than the diameter of the capillary opening in the ampoule. The tetrahalide molecules

flowed out essentially under equilibrium conditions, and the outlet orifice had sharp edges; therefore the effusion of the tetrahalide vapor obeyed Knudsen' s cosine law,

$$ds = \frac{d\omega}{\pi} \cos x,$$

where ds is the probability with which a molecule, passing through the outlet

orifice, will be found in an element of solid angle. The angle between $d\omega$ and the normal (axis) of the ampoule orifice is denoted by x. Knowing the distance from the ampoule nozzle to the target (10–15 mm) and taking the angles of the capillary opening to be straight, it is possible to calculate what the width of the target strip must be so that at least 99.9% of the effusing tetrahalide molecules would strike its surface. Under our conditions this value was 10–15 mm.

Table 2

Dependence of the decomposition coefficients of zirconium and hafnium tetrahalides on the surface temperature

Tetrahalide	Target temp., °C	Decomp. coeff., %	Tetrahalide	Target temp., °C	Decomp. coeff., %
$HfCl_4$	1500	0	HfJ_4	1500	96
$HfCl_4$	1470	0	HfJ_4	1480	90
$ZrCl_4$	1495	5	HfJ_4	1420	72
$ZrCl_4$	1480	4	HfJ_4	1280	53
$ZrCl_4$	1445	0	HfJ_4	1160	20
$HfBr_4$	1500	50	HfJ_4	1115	20
$HfBr_4$	1465	37	HfJ_4	1050	0
$HfBr_4$	1380	25	ZrJ_4	1495	100
$HfBr_4$	1325	8	ZrJ_4	1460	100
$HfBr_4$	1280	3	ZrJ_4	1410	98
$HfBr_4$	1245	0	ZrJ_4	1400	92
$ZrBr_4$	1500	59	ZrJ_4	1335	90
$ZrBr_4$	1480	50	ZrJ_4	1265	61
$ZrBr_4$	1430	40	ZrJ_4	1195	50
$ZrBr_4$	1365	27	ZrJ_4	1150	46
$ZrBr_4$	1320	20	ZrJ_4	1070	27
$ZrBr_4$	1245	5	ZrJ_4	1000	7

The results of the investigation are presented in Table 2. The number of effusing molecules was calculated from the loss in weight of the ampoule, and the number of decomposed molecules from the weight of the disk obtained. Their ratio gave the value of the decomposition coefficient.

As is evident from the data obtained, at a temperature of 1500° only the molecules of zirconium tetraiodide decompose completely, whereas the decomposition of hafnium tetraiodide proceeds to 90%. Zirconium and hafnium tetrabromides decompose by 68 and 61%, respectively. The tetrachlorides of both elements undergo almost no dissociation. In all cases, the hafnium tetrahalides have greater thermal stability in comparison with the analogous zirconium compounds. Moreover, the difference in thermal stability is expressed to a considerably greater degree for the iodides than for the bromides. Thus, for example, at 1460° the difference in the decomposition coefficients for the iodides is 15%, and

for the bromides 7%. In all cases the value of the decomposition coefficient is directly proportional to the target temperature (Fig. 2). The thermal stability of the tetrahalides is, in general, consistent with the values of their enthalpies of formation.

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