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# CHEMISTRY

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## Abstract

## Full Text

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# MASS-SPECTROMETRIC STUDY OF THE SUBLIMATION OF GERMANIUM DIOXIDE

*(Presented by Academician A. N. Terenin, February 5, 1958)*

The study of germanium compounds that form a surface film is attracting increasing attention, since the properties of this metal as a semiconductor depend to a high degree on the state of its surface. From this point of view, knowledge of the thermodynamic characteristics of germanium dioxide, in particular the vapor pressure and heat of sublimation, is very important, all the more so because until quite recently these quantities had not been measured at all.

Davydov <sup>(1)</sup> measured, by the Knudsen effusion method, the pressure of saturated vapor over solid GeO<sub>2</sub>. The heat of sublimation in the range 886—980° was found to be 29.5 kcal/mol, and in the range 1025—1078°, 71.5 kcal/mol. The author attributes such a sharp change in the heat of sublimation to a phase transition at 1000°.

In carrying out the present work, mass spectrometers of the MS-1 and MS-4 types were used. The ion source did not differ in principle from that described by Aldrich <sup>(2)</sup>. Germanium dioxide was deposited on a platinum evaporator, which consisted of a strip spot-welded to nichrome holders. The vapor entered through a small opening into the ionization chamber, where it was ionized by electron impact. The temperature of the evaporator was measured with a platinum-platinum-rhodium thermocouple welded to it.

In the source used by us, the magnitude of the ion current is related to the vapor pressure of the substance by the relation <sup>(3)</sup>:

$$I^+ = \frac{kP}{T}.$$

The coefficient  $k$  depends on the design parameters of the instrument and on the effective ionization cross section; therefore its direct determination, and hence that of the vapor pressure of the substance, is difficult. Nevertheless, the heat of sublimation can be determined by measuring the dependence of the ion current on temperature and plotting the graph in the coordinates  $\lg(I^+T) = f\left(\frac{1}{T}\right)$ .

In preliminary experiments we determined the heat of sublimation of silver, for which numerous and reliable data are available in the literature. According to

Fig. 1. Mass spectrum of vapor over germanium dioxide

Figure 1: Fig. 1. Mass spectrum of vapor over germanium dioxide

our data,  $\Delta H$  of sublimation in the range 680—820° is  $66.5 \pm 0.5$  kcal/mol, which is in good agreement with the values 65.5 kcal/mol (<sup>4</sup>) and 68 kcal/mol (<sup>5</sup>). In the mass spectrum of silver vapor we observed only  $\text{Ag}^+$  ions.

Germanium dioxide was obtained by dissolving metallic germanium in a nitric-acid solution of hydrogen peroxide. The  $\text{GeO}_2$  was then recrystallized from hot water.

Table 1

Ionizing voltage, V	$\text{Ge}_3\text{O}_3^+$	$\text{Ge}_2\text{O}_2^+$	$\text{Ge}_2\text{O}^+$	$\text{GeO}^+$	$\text{Ge}^+$	$\text{O}_2^+$	$\text{O}^+$
	70	1	1.15	0.3	0.95	0.56	2.6
40	1	0.85	0.22	0.55	0.3		
15	1	0.48	0.13	0.42	0.19		

Table 1 gives data on the mass spectrum of the vapor over  $\text{GeO}_2$ . The measurements were made at an evaporator temperature of 1000°, an electron-emission current of 1.5 mA, and three different values of the ionizing voltage. In compiling the table we summed the intensities of the ion currents corresponding to the individual germanium isotopes and referred them to the current of  $\text{Ge}_3\text{O}_3^+$  ions, whose intensity was taken as unity.

Fig. 1. Mass spectrum of vapor over germanium dioxide

We also observed  $\text{Ge}_3\text{O}_2^+$  and  $\text{GeO}_2^+$  ions, whose current amounted to about 0.5% of the magnitude of the  $\text{Ge}_3\text{O}_3^+$  current. Figure 1 shows a portion of the mass spectrum corresponding to the  $\text{Ge}_2\text{O}_2^+$  and  $\text{Ge}_3\text{O}_3^+$  ion groups.

For some groups of the mass spectrum, the dependence of the ion-current intensity on temperature was measured (the measurements were made at the largest peak in the group). The enthalpy values (in kcal/mole), calculated from the slopes of the straight lines  $\lg(I^+T) = f\left(\frac{1}{T}\right)$ , proved to be as follows:

Ion	$\text{Ge}^+$	$\text{GeO}^+$	$\text{Ge}_2\text{O}_2^+$	$\text{Ge}_3\text{O}_3^+$	$\text{O}_2^+$	$\text{O}^+$
$\Delta H_T$	$106 \pm 5$	$101 \pm 2$	$108 \pm 1$	$113 \pm 5$	$110$	

It was not possible to measure the temperature dependence of the  $\text{GeO}_2$  ion current because of its very low intensity.

Within the error of our measurements we did not observe any breaks in the straight lines for the dependence  $\lg(I^+T) = f\left(\frac{1}{T}\right)$ . The elasticity of the  $\text{Ge}_3\text{O}_3$  vapor can be estimated by comparing the ion currents  $\text{Ge}_3\text{O}_3^+$  and  $\text{Ag}^+$ . The ratio of the effective ionization cross sections for the  $\text{Ge}_3\text{O}_3$  molecule and the Ag atom is close to 4:1 <sup>(6)</sup>. We may then assume:

$$I_1^+T_1 = \frac{I_2^+T_2}{4} = kP,$$

where  $I_1^+T_1$  and  $I_2^+T_2$  refer respectively to the ion currents  $\text{Ag}^+$  and  $\text{Ge}_3\text{O}_3^+$ . An equality of this kind held in our ion source, for example

at  $T_1 = 1073^\circ$  and  $T_2 = 1338^\circ$ . For silver, a temperature of  $800^\circ$  corresponds to a vapor pressure of  $6 \cdot 10^{-5}$  mm Hg. <sup>(4,5)</sup>. Consequently, the vapor pressure of  $\text{Ge}_3\text{O}_3$  at a temperature of  $1065^\circ$  will be, approximately, on the order of  $2 \cdot 10^{-5}$  mm Hg.

Thus, the evaporation of germanium dioxide with respect to the composition of the gas phase proves to be analogous to the case of evaporation of  $\text{SiO}_2$  <sup>(7,8)</sup>, when predominantly  $\text{SiO}$  molecules were observed in the vapor. The stability of  $\text{GeO}$  toward disproportionation was shown earlier by calculation <sup>(9)</sup>.

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

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