The Rate of Vaporization from the Surface of Molten Germanium Dioxide

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Following the measurement of the oxygen diffusion rate in the solid germanium dioxide,[1] the same experiment was tried on the melt. As it was noticed that the vaporization from the melt was much faster than that from the crystal, and as the movement of the boundary surface could not be ignored, the rate of the vaporization, or the movement of the boundary between the melt and the vapor, was measured. In order that the results could be employed for diffusion measurements, the measurements were made under an oxygen pressure of about 150 mmHg, which corresponds to the partial pressure of oxygen in air. The results obtained seem reasonable compared to those for relative substances.

As a starting material, electronic grade germanium dioxide powder made by the Baker & Adamson Co. was employed. The melting points of the substance are 1116°C for the hexagonal, and 1086°C for the tetragonal crystal respectively.[2] The former form is the high temperature stable phase, and the latter, the low temperature stable phase. When the powder is melted down in the air by an electric furnace, it forms a white translucent glass including a lot of air. To expel the bubbles from the glass, it was heated for one hour each at 1150, 1350, 1400, 1480, 1496 and 1560 °C. The best condition was found experimentally to be 1500±10°C. At higher temperatures than this, much of the substance is lost by evaporation. The transparent bubble-free glass thus obtained was used as a sample.

The rate of boundary movement was calculated from the weight decrease of the sample kept in a platinum dish (Fig. 1) during heating by a high frequency furnace working at 10,000 cycles per second. The temperature of the sample was measured by a potentiometer-type optical pyrometer* made by the Leeds & Northrop Co. (Catalog No. 8622c). Absorption by the window made by a pyrex glass plate was corrected employing the experimental curve (Fig. 2). To avoid the condensation of germania and platinum on the surface of the observation glass window, it was protected by a sheet of iron plate held by a magnet outside, and the iron plate was slid aside only during the temperature observation. When this step was taken, no change in the correction curve was observed before or after the run. The other parts of glass, which had not been protected, changed their absorptivity after the run.

The results of the experiment are shown in Table I. The weight loss of the platinum dish was smaller than the experimental error. The relations between the reciprocal of the absolute temperature ($1/T$°K) and the logarithm of

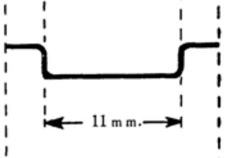

Fig. 1. Size and form of the platinum evaporation vessel.

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[1] T. Tokuda and W. D. Kingery, *J. Appl. Phys.*, **34**, 2104 (1963).

[2] Gmelin, "Handbuch d. Anorg. Chemie, Germanium," Erg. Bd., 498; A. W. Laubengayer and D. S. Morton, *J. Am. Chem. Soc.*, **54**, 2303, 2309 (1932).

* It is more accurate and reliable than the amperemeter-type optical pyrometer.

TABLE I. RATE OF VAPORIZATION FROM THE SURFACE OF MOLTEN GeO_2

Run No.	No. 206	No. 201	No. 207	No. 204	No. 203
Initial weight, g.	0.2519	0.1620	0.2244	0.2540	0.3624
Weight loss observed, mg./hr.	0.663	6.75	32.0	50.7	242.
Vaporization rate, mol./sec. cm^2	1.852×10^{-9}	1.884×10^{-8}	8.940×10^{-8}	1.410×10^{-7}	6.787×10^{-7}
Decrease in thickness, cm./hr.	0.0002329	0.002368	0.011224	0.01778	0.08492
Temperature observed, °C	1140±13	1240±13	1294±4	1360±10	1439±20
Temperature corrected, °C	1171	1262	1320	1390	1478

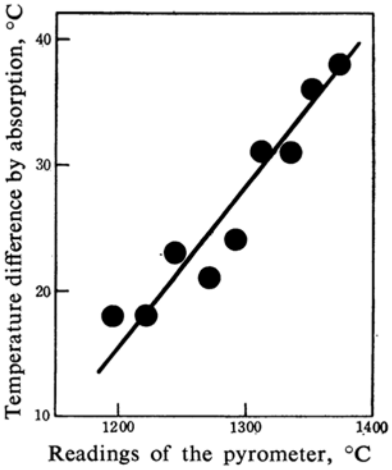

Fig. 2. Correction curve for pyrex glass absorption.

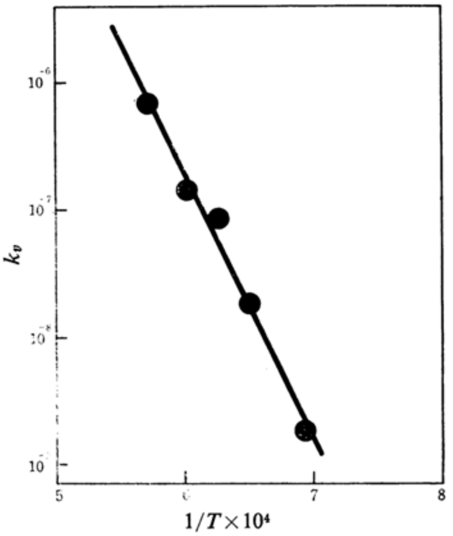

Fig. 3. Rate contstant of evaporation vs. $1/T$.

the rate of vaporization are shown in Fig. 3. The rate constant for the vaporization can be expressed by the following formula;

$$k_v=4.07\times10^6\exp(-96{,}000/\boldsymbol{R}T)$$

According to Condon,[3] the activation energies of vaporization for the one oxygen atom in both silicon oxide and boron oxide are 22 kcal. The one in germanium(IV) oxide which we obtained is 96/4=24 kcal. The value we obtained here seems quite reasonable. Assuming that Eyring's equation

$$k_v=(1/6)e\lambda^2(\boldsymbol{k}T/\boldsymbol{h})\exp(\Delta S^{\ddagger}/\boldsymbol{R})$$

is applicable in this case, where $\boldsymbol{k}$ is the Boltzmann constant, $\boldsymbol{h}$ is the Planck constant, and $\boldsymbol{R}$ is the gas constant, and where the jump distance, λ, is about 2.7Å, the entropy of vaporization, $\Delta S^{\ddagger}$, can be calculated. Around the melting point (1116°C), it is calculated as follows; $\Delta S^{\ddagger}=39.6$ cal. mol^{-1} deg^{-1}.

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[3] E. U. Condon, *Am. J. Phys.*, **22**, 132 (1954).