The Vapor Pressure of Germanium Dioxide

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Though germanium dioxide is expected to be more or less volatile at higher temperatures, the exact magnitude of its vapor pressure is not known. Moreover, the thermodynamic properties of the dioxide have been but little studied. To make a contribution to the chemistry of germanium, we have determined the vapor pressure of solid germanium dioxide; the measurements were made by Knudsen's effusion method over the temperature range from 1,040°C up to its melting point.

There is no evidence for the existence of gaseous germanium dioxide. The most important gas species over the solid dioxide around these temperatures is considered to be monoxide vapor[1]; so the vaporization can be regarded as the dissociation reaction,

$$GeO_2\,(c)^* = GeO\,(g.) + 1/2\ O_2\,(g.). \qquad (1)$$

The possibility of other reactions, for instance the dissociation into constituent elements, is excluded from the free energy consideration; and, as the non existence of solid monoxide has been discussed by so many investigators, there may be no room for it as a dissociation product.

Experimental

Apparatus and Procedure.—The apparatus was the same as that used in the previous investigations carried out in this laboratory; the measuring technique was slihgtly modified as described elsewhere[2]. The weight of vapor effusing through an orifice out from the quartz Knudsen cell is measured by means of a microthermobalance enclosed in the vacuum system. The vapor pressure is then calculated from the relation

$$p = \sqrt{\frac{2\pi RT}{M}} \cdot \frac{1}{A} \cdot \frac{G}{\tau} \qquad (2)$$

where G is the weight loss of the sample in duration of τ seconds, A the orifice area and M the molecular weight of the gas molecule.

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[1] L. Brewer *Chem. Rev.*, **52**, 62 (1953).

[2] E. Shimazaki and T. Wada, This Bulletin, **29**, 294 (1956).

* In this paper, GeO_2(c) means crystalline germanium dioxide of hexagonal α-quartz structure.

In this investigation, the mean molecular weight of two gaseous components was taken as M, the germanium monoxide vapor being assumed to be unimolecular. Inserting the values of constants and of the mean molecular weight, together with $A=4.19\times10^{-3}\,\text{cm}^2$, we obtain from equation (2)

$$p\ (\text{mmHg})=489.99\frac{G}{\tau}\sqrt{T}. \tag{3}$$

The Sample.—The sample of germanium dioxide, stated 99.99% pure, was of the make of Deutsche Otavi Eisenbahngesellschaft, and was used without any further purification. Prior to the measurements, it was heated in the air above 1,000° for several hours to remove any absorbed gases or moisture. This microcrystalline white powder, as well as the residue remaining in the cell after the experiment, showed nothing but the pattern of germanium dioxide of hexagonal quartz structure in the X-ray diffraction studies.

The coincidence of the cell temperature with the thermometer reading was ensured by the fact that the sample held at the temperature just above its melting point (1,116°C) was in glassy appearance in the quartz cell, indicating that it had melted.

Results and Discussion

The results of the experiment are summarized in Table I and plotted in Fig. 1. By means of the method of least squares, the results are expressed by equation (4), corresponding to the straight line in the $\log p$ vs. $1/T$ plot in Fig. 1.

$$\log p_{\text{mm.}}=-\frac{25,517}{T}+16.245 \tag{4}$$

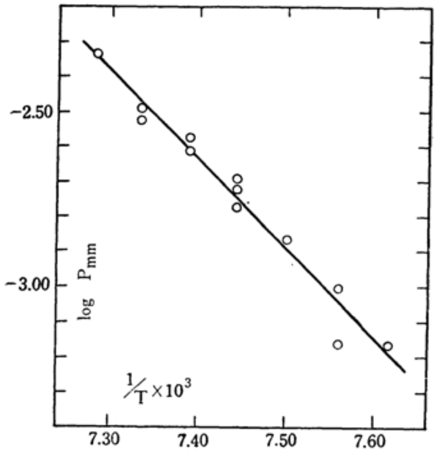

Fig. 1.

By differentitation of equation (4) with respect to $1/T$, or from the inclination of the straight line in Fig. 1, the heat of reaction (1) is obtained as

$$\varDelta H_T=116.7\pm0.2\ \text{kcal./mol.}$$

TABLE I

Tem. T°K	Loss in Weight $G\times10^3$ g.	Duration τ sec.	Vapor Pressure $p\times10^3$ mmHg.	$\log p+4.$
1,313	0.827	21,600	0.680	0.832
1,323	0.808	18,000	0.689	0.838
〃	1.000	〃	0.990	0.996
1,333	1.365	18,000	1.356	1.132
1,343	1.173	12,600	1.672	1.223
〃	2.038	18,000	2.033	1.308
〃	1.500	14,400	1.870	1.272
1,353	1.327	9,000	2.657	1.424
〃	1.923	14,400	2.407	1.381
1,363	2.384	14,400	2.995	1.476
〃	2.557	〃	3.212	1.506
1,373	2.769	10,800	4.655	1.668

The orifice area $A=4.19\times10^{-3}\,\text{cm}^2$.

The free energy and the entropy change are also calculated,

$$\varDelta G_T=34.0\ \text{kcal./mol.}$$

$$\varDelta S_T=61.1\ \text{kcal./mol./deg.}$$

where underscript T denotes the mean temperature in the experiment. To construct the free energy equation, the following heat capacity equations were used:

$$\text{GeO}_2(\text{c})\,^{3)}\quad C_p=11.2+7.17\times10^{-3}T$$

$$\text{O}_2(\text{g})\,^{3)}\quad C_p=7.16+1.00\times10^{-3}T-0.40\times10^5T^{-2}$$

$$\text{GeO}(\text{g})\quad C_p=\frac{7}{2}R+C_{vib}$$

where C_{vib} is the heat capacity resulting from the atomic vibration in the gaseous GeO molecule and is equal to the Einstein heat capacity function $E(\theta/T)$.

Hence

$$\varDelta C_p=-0.67-6.67\times10^{-3}T-0.20\times10^5T^{-2}+E(\theta/T)$$

On integration we botain

$$\varDelta H=\int_0^T\varDelta C_p\mathrm{d}T=\varDelta H_0-0.67T-3.335\times10^{-3}T^2+0.20\times10^5T^{-1}+\int_0^T E\left(\frac{\theta}{T}\right)\mathrm{d}T \tag{5}$$

where $\varDelta H_0$ is the constant of integration. Then the free energy equation is obtained as

$$\varDelta G=\varDelta H_0+0.67T\ln T+3.335\times10^{-3}T^2+0.10\times10^5T^{-1}-T\int_0^T\frac{\mathrm{d}T}{T^2}\int_0^T E\left(\frac{\theta}{T}\right)\mathrm{d}T+JT \tag{6}$$

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3) K. K. Kelley, *Bur. Mines Bulletin*, No. 476 (1949).

where J is another constant of integration.

These two constants were evaluated in the usual manner. With the relation

$$\Delta G = -RT \ln p_{\mathrm{atm}} = -4.575T \log p_{\mathrm{atm}}$$

equation (6) is changed to

$$\begin{aligned}\Sigma = & -4.575 \log p - 0.67 \times 2.303 \log T \\ & -3.335 \times 10^{-3} T - 1 \times 10^{4} T^{-2} \\ & + \int_0^T \frac{\mathrm{d}T}{T^2} \int_0^T E\left(\frac{\theta}{T}\right) \mathrm{d}T = \frac{\Delta H_0}{T} + J\end{aligned}$$

$E(\theta/T)$ was evaluated for each temperature from the table[4] as $E(\theta/T) = 1/3\, C_v$ with the characteristic temperature $\theta = 1{,}411$ which in turn was calculated from Barrow's spectroscopic data[5]. Integration and double integration of $E(\theta/T)$-function were carried out graphically. By means of the method of least squares using twelve Σ functions, ΔH_0 and I were obtained:

$$\Delta H_0 = 122{,}122 \pm 285$$

and $$J = -73.583$$

With these values, the heat of reaction, the free energy and the entropy change at 298°K were calculated from equations (5) and (6) as follows:

$$\Delta H_{298} = 121.7 \pm 0.3 \text{ kcal./mol.}$$

$$\Delta G_{298} = 101.7 \text{ kcal./mol.}$$

$$\Delta S_{298} = 67.3 \text{ cal./mol./deg.}$$

The heat of reaction can also be obtained by combining the thermal data from the literature (Table II).

TABLE II

Reaction	ΔH_{298}, kcal.
$GeO_2(s) = Ge(s) + O_2(g)$	128.3±1.0[6]
$Ge(s) = Ge(g)$	91.5±3.0[7]
$1/2\ O_2(g) = O(g)$	59.2
$Ge(g) + O(g) = GeO(g)$	−159.0[8]
$GeO_2(s) = GeO(g) + 1/2\, O_2(g)$	120.0±4 kcal

It must be remembered that the heat of formation of solid germanium dioxide, 128.3 kcal., is referred to its amorphous state. The heat of transition GeO_2 (amorph.) $= GeO_2$(cryst.) is unknown, but considering the case of silicon dioxide, it may not be bold to take it as high as 2 kcal. Adding this, the heat of reaction is obtained as 122.0 kcal., which is in good accord with our experimental value of 121.7 kcal.

The heat of dissociation of gaseous germanium monoxide cited above, 159 kcal., was calculated by Herzberg from the spectroscopic evidence by Birge-Sponer linear extrapolation. Though the applicability of the linear extrapolation to all oxides of group-4 elements was discussed by Brewer[1,9], our experimental result also suggests that Herzberg's value is preferable to Gaydon's, 127±27 kcal.

From $\Delta S_{298} = 67.3$ e. u., together with the entropy values from the literature[10] $S_{298} = 49.01 \pm 0.1$ e. u. for oxygen and $S_{298} = 53.55 \pm 0.1$ e. u. for gaseous germanium monoxide, the entropy of solid germanium dioxde is obtained as $S_{298} = 10.8 \pm 1.0$ e. u. This is in fair agreement with the estimated value 11.5 which was evaluated by Bues and von Wartenberg, by interpolation from normal entropies of dioxides of silicon and tin[11].

Summary

The apparent vapor pressure of solid germanium dioxide, or the dissociation pressure for the reaction $GeO_2(c) = GeO(g) + 1/2\, O_2(g)$, was measured over the temperature range 1,040–1,100°C by the Knudsen's effusion method; the results are expressed by equation (4).

From the free energy equation, the heat of reaction, the free energy and the entropy change of the reaction were calculated as $\Delta H_{298} = 121.7 \pm 0.3$kcal./mol., $\Delta G_{298} = 101.7$ kcal./mol. and $\Delta S_{298} = 67.3$ e. u., respectively. The heat of reaction is in good agreement with the value calculated from accessible thermal data. The normal entropy of solid germanium dioxide was calculated as $S_{298} = 10.8 \pm 1.0$ e. u., which is in agreement with the computed value obtained by Bues and von Wartenberg.

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[4] Landolt-Börnstein, Tabellen, Erg. I., p. 702.

[5] R. F. Barrow, *Proc. Phys. Soc.*, **56**, 204 (1944).

[6] J. P. Coughlin, *Bur. Mines Bulletin*, No. 542 (1954).

[7] A. W. Searcy and R. D. Freeman, *J. Chem. Phys.*, **23**, 88 (1955).

[8] G. Herzberg, "Molekülspektren und Molekülstruktur." Th. Steinkopf, Dresden und Leipzig, 1939, 336.

[9] L. Brewer and D. F. Mastick, *J. Chem.* Phys., **19**, 834 (1951).

[10] K. K. Kelley, *Bur. Mines Bulletin*, No. 477 (1951).

[11] W. Bues and H. von Wartenberg, *Z. anorg. allg. Chem.*, **266**, 281 (1951).