Vapor Pressure of Germanium Monosulfide

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Germanium monosulfide has a relatively high volatility, and hence it can be removed from germanite or other minerals containing germanium sulfide by vaporizing it in reducing atmosphere[1]. However, the quantitative value of vapor pressure has not yet been reported.

In the present work, the vapor pressure of germanium monosulfide is determined by means of Knudsen's effusion method over the temperature range from 338°C to 399°C, and the heat, free energy, and entropy of sublimation are calculated from the experimental results obtained.

As Kundsen has first derived[2], the weight of vapor G effusing in a time τ through an area A is related to the pressure p by

$$p=\sqrt{\frac{2\pi RT}{M}}\cdot\frac{G}{\tau}\cdot\frac{1}{A}, \tag{1}$$

where R is the gas constant, T is the absolute temperature and M is the molecular weight of effusing vapor. The method based on the above relation is the most reliable one when the vapor pressure to be measured is lower than 10^{-2} mmHg.

It has been already confirmed that the dissociation of germanium monosulfide such as

$$\mathrm{GeS(s)} \rightleftarrows \mathrm{Ge(s)}+\frac{1}{2}\mathrm{S_2(g)}, \tag{2}$$

does not practically occur at the temperature of this experiment. According to the recent study of Ono and Sudo[3], the dissociation pressure P_{S_2} of the above reaction is only 10^{-13} atm. even at 415°C.

The molecular association in effusing vapor is not considered, regarding the molecular formula as GeS. Although there is no direct evidence, this assumption is supported by the measurement on the density of vapor at 1100°C and 1500°C[4], and by the spectroscopic information on the gaseous germanium monosulfide[5].

Experimental

Apparatus and Procedure.—The apparatus used for determination of vapor pressure is the same as that used by Niwa in the studies on the vapor pressure of alkali halides[6]. It is essentially composed of a quartz cell having a small orifice from which the vapor is effused, and a microbalance by which the weight of effused vapor is determined. Details have been described in Niwa's original paper.

The original experimental procedure is modified in some respect: In the present work the decrease of weight during a certain time is measured by the microbalance which is calibrated in advance, whereas in the original paper the time required to effuse a certain quantity of a sample, a quantity corresponding to the rider, was measured. There is no essential difference, however, between these two procedures.

The accuracy of experiment is not greatly different from Niwa's, in which the maximum error is estimated as 2.6% at most.

Material.—Germanium monosulfide used was prepared by treating metallic germanium with hydrogen sulfide. Metallic germanium was obtained by reduction of germanium dioxide having a purity of 99.999% with hydrogen. The powder

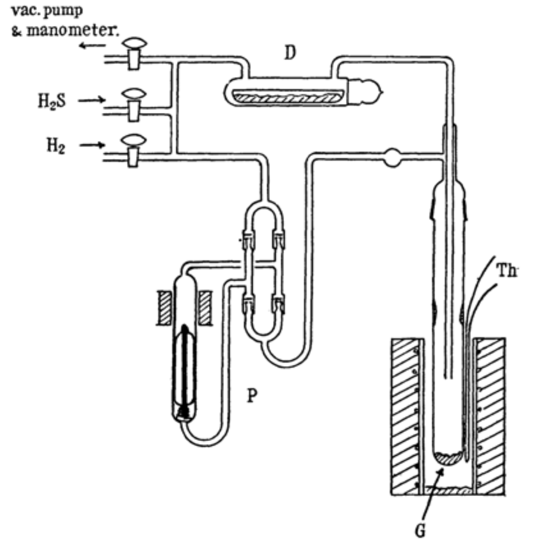

Fig. 1. Apparatus for preparation of GeS.
D; Phosphorous pentoxide.
P; Circulation pump.
Th; Pt-PtRh thermocouple.
G; Powder of germanium metal.

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of germanium thus obtained was taken in a reaction tube of Telex glass with 2 cm. diameter and 20 cm. long, which is connected to vacuum pump, circulation pump, and storage bulbs of hydrogen sulfide and hydrogen, as shown in Fig. 1. Then, after the treatment with hydrogen at 600°C to remove completely the rest of oxygen, hydrogen sulfide was introduced up to about 100 mmHg and was circulated gently at 550°C. As reaction proceeded, germanium monosulfide was condensed on the cold part of reaction tube.

Germanium monosulfide thus prepared has the appearance of dark grey with metallic lustre, whereas it becomes reddish brown when it is finely powdered[7]. The X-ray powder pattern is consistent with the crystal structure of germanium monosulfide which is proposed by Zachariasen[8] such as orthorhombic with lattice parameters of a=4.29, b=10.42, and c=3.64 Å, as shown in Table I. The lines of metallic germanium, germanium dioxide, or germanium disulfide are not observed. Germanium disulfide may be the only possible impurity. But its vapor pressure is far less than that of monosulfide[9], so it does not markedly affect the results even if it is present.

TABLE I

X-RAY DIFFRACTION PATTERN OF GERMANIUM MONOSULFIDE

obs.		(hkl)	d (calc.)	Intensity observed by Zachariasen[8].
d (A)	Intensity.			
5.26	vvw	(020)	5.21	vvw
4.00	vw	(110)	3.97	vw
3.34	st	(120)	3.32	m
3.00	mw	(012)	2.97	m
2.79	mw	(101)	2.77	—
2.70	st	(111)	2.68	st
2.63	vst	(040)	2.61	vvst
2.18	m	(131)	2.17	st
2.11	w	(210)	2.10	mst
1.910	mw	(141)	1.899	st
1.888	vw	(150)	1.876	m⁻
1.824	m	(230)	1.826	m
1.746	vw	(060)	1.737	vw
1.669	m	(151)	1.689	st
1.639	vw	(231)	1.632	w
1.618	vw	(160)	1.610	m
1.598	vw	(122)	1.590	m
1.578	vw	(061)	1.568	m
1.497	w	(250)	1.496	m
1.386	w dif.			
1.311	w			

Ono and Sudo[3] have shown that the decomposition of germanium monosulfide to form disulfide and metal such as

$$2\mathrm{GeS(s)} \rightleftarrows \mathrm{GeS_2(s)} + \mathrm{Ge(s)}, \tag{3}$$

is possible at the temperature below 388°C. After the measurement, however, the residue remaining in the cell was reexamined by X-ray diffraction, and it was confirmed that the decomposition like the above had not occurred.

Results

Vapor pressure.—The experimental results on G and τ for various temperatures, and vapor pressures calculated according to equation (1) are recorded in Table II.

TABLE II

RESULTS OF EXPERIMENTS AND VAPOR PRESSURE OF GERMANIUM MONOSULFIDE

Temp. °C	Decrease of weight, G, (mg.)	Duration, τ, (sec.)	Vapor pressure p, (mmHg)
399	5.48_0	3780	12.73×10^{-3}
387	2.73_5	3600	6.61 〃
382	3.38_4	5400	5.44 〃
378	1.88_0	3720	4.37 〃
375	1.95_2	5300	3.18 〃
368	0.95_4	3630	2.26 〃
364	1.76_4	7200	2.10 〃
361	0.63_6	3000	1.82 〃
356	0.54_9	3600	1.30 〃
348	0.65_1	6600	0.83 〃
338	0.34_7	6300	0.46 〃

The area of orifice is 4.94×10^{-3} cm.

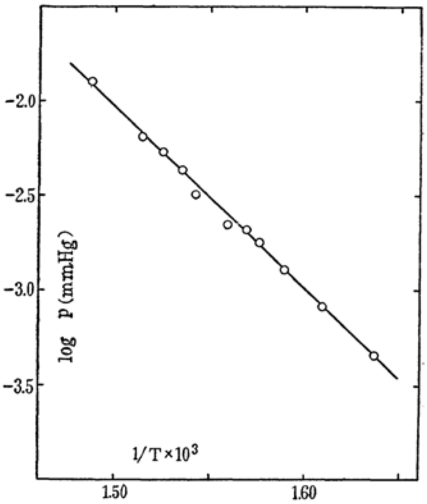

Fig. 2. Logarithms of vapor pressures of GeS, plotted against 1/T.

As shown in Fig. 2, the logarithms of vapor pressures are linearly related against the reciprocals of the absolute temperature. This straight line is represented by the following equation;

$$\log p_{(\mathrm{mmHg})} = -\frac{9591}{T} + 12.357. \tag{4}$$

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Calculation of Thermodynamic Values.—The heat of sublimation ΔH_T, free energy change of sublimation ΔG_T, and entropy change of sublimation ΔS_T are calculated according to well-known thermodynamic relations:

From Clausius-Clapeyron's equation,

$$\Delta H_T = -R\frac{\mathrm{d}\ln p}{\mathrm{d}(1/T)}. \qquad (5)$$

As to free energy change of sublimation,

$$\Delta G_T = -RT\ln p_{(\mathrm{atm.})}, \qquad (6)$$

and as to entropy change of sublimation,

$$\Delta S = \frac{\Delta H_T - \Delta G_T}{T}. \qquad (7)$$

The values of these thermodynamic functions are obtained as shown in Table III.

TABLE III

HEAT, FREE ENERGY, AND ENTROPY OF SUBLIMATION OF GERMANIUM MONOSULFIDE AT THE TEMPERATURE FROM 338° TO 399°C

ΔH_T, kcal./mol.	ΔG_T, cal./mol.	ΔS_T, cal./deg.mol.
43.9	43869–43.343T	43.3

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