On the Dissociation Pressures of Germanium Sulfides

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On the Dissociation Pressures of Germanium Sulfides*

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Synopsis

Measurements on the equilibria in the hydrogen reductions of germanium sulfides, viz., GeS_2 and GeS synthesized in laboratory, were carried out over the temperature range from 390° to 485°C using the flow method. From the observed data, simple equations for representing the correlation of log p_{S_2} with $1/T$ were deduced. Basing themselves on the present numerical data and other published papers, the behaviour of germanium in practical processes of smelting of sulfide ores was discussed.

I. Introduction

Germanium, known as a semiconductor, has come into the limelight since the report concerning a transistor from Bell Telephone Laboratories, U. S. A., appeared in June 1948. For the purpose of recovering germanium from its ores or coal—including lignite—various attempts were made and a few methods have been already industrialized.(1)~(8)

Unfortunately this element is widely distributed in the earth's crust and is known as a toxic element in the process of zinc smelting. In addition it had no special use. From these points of view, germanium had not been recognized as an object of smelting. Therefore the wet process adopted from analytical chemistry was employed for its recovery. Now, since its value has been recognized, it may be desirous to establish a proper process for recovery of this element. In the first place, the following studies were undertaken with an object of knowing the behaviour of germanium in its ores at high temperature.

Basing on the fact that nearly all the ores containing germanium are sulfides, the present authors gave attention to their component minerals and learned the next points. The minerals with a high content of germanium, viz., argyrodite ($Ag_2S \cdot GeS_2$), canfieldite ($4Ag_2S \cdot (Ge \cdot Cu)S_2$) and germanite ($10Cu_2S \cdot 4GeS_2 \cdot As_2S_3$), are thought to contain this element in the form of GeS_2. Accordingly the knowledge of the behaviour of GeS_2 and other compounds derived from it seems to be

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* The 66th report of the Research Institute of Mineral Dressing and Metallurgy.

(1) H. C. Torrey and C. A. Whitner, *Crystal Rectifier*, (1946).

(2) K. Sudo, J. Electrochem. Soc. Japan (in Japanese), **17** (1949), 238.

(3) Institution of Mining and Metallurgy, *The Refining of Non-Ferrous Metals*, (1950), 51.

(4) M. Inagaki, J. Electrochem. Soc. Japan (in Japanese), **20** (1952), 595.

(5) A.P. Thompson and J.R. McGrave, J. Metals, **4** (1952), 1132; Mining Eng., **5** (1953), 42.

(6) K. Ono, J. Japan Inst. Metals (in Japanese), **11** (1953), A257.

(7) A. J. W. Headlee, Mining Eng., **5** (1953), 1011.

(8) R. C. Chirnshide and H. J. Chiley, G. E. J., **19** (1952), 94; C. A., **46** (1952), 6561; cf. J. Metals, **5** (1953), 979.

important for understanding the concentrating process of germanium in the smelting of its ores. Beside GeS_2 described above, GeS having a distorted NaCl type structure is reported as a form of germanium sulfides.(9)

In the present experiment, the authors synthesized above sulfides in this laboratory and their reduction equilibria with hydrogen were measured by means of the flow method. From the results obtained, the temperature dependence of the dissociation pressures of germanium sulfides were determined. Furthermore, basing themselves on these data, the behaviour of germanium in the processes of smelting of sulfide ores was discussed.

II. Experimental apparatus and procedure

The apparatus was the same as that used for measurements of reduction equilibria of metallic sulfides with hydrogen as a part of fundamental researches on smelting of sulfide ores by one of the present authors.(10) Also the same procedure of flow method as in the previous studies was followed.

III. On the equilibrium in the reduction of GeS_2 with hydrogen

1. Meterial

Using metallic germanium with a purity of 99.999 per cent made in England and refined sulfur, the present samples were synthesized in dry process. Namely, after weighing and mixing both elements in the ratio of the components in GeS_2, about 1 to 2 g of the mixture was charged into a hard glass tube with a closed end 10 mm in outer diameter. After evacuating the tube with a rotary vacuum pump, the other open end was also sealed. The sample in the tube was slowly heated with a gas burner and the combination of both elements was completed. Thereafter it was heated sowly to 600°C in an electric furnace and kept there for 24 hours until the existence of free sulfur was hardly recognized. Then the tube was taken out from the furnace. In this case, such a rapid heating of the closed tube as employed by Hirahara(11) for synthesis of Cu_2S seems to be liable to accompany explosion at the first stage of the change. After cooling it to room temperature, one end of the closed tube was broken and the sample in it was taken out. Its appearance was like inpure sulfur solidified from molton state on the surface.

The powder ground with an agate mortar had a white or a light yellow color which seemed to show the presence of free sulfur. Accordingly the fine powder was placed on a silica boat which was put into an silica reaction tube and while it was being evacuated with a rotary vacuum pump, it was slowly heated to 450°C and kept there for an hour. After allowing to cool in the furnace to room temperature, it was used for the present experiment.

The sulfur content of the sample thus prepared was determined to be 46.12 per

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(9) R. Kiriyama, ***Kôzômukikagaku*** (in Japanese), **1** (1952), 133, 138.

(10) K. Sudo, Sci. Rep. RITU, **A2** (1950), 305.

(11) E. Hirahara, Ôyô-butsuri (in Japanese), **18** (1949), 187.

cent (theoretical content is 46.91 per cent) by gravimetric analysis. Its X-ray diffraction pattern is given in Phot. 1, which shows crystallization of the sample induced by holding it at a high temperature for a long time.

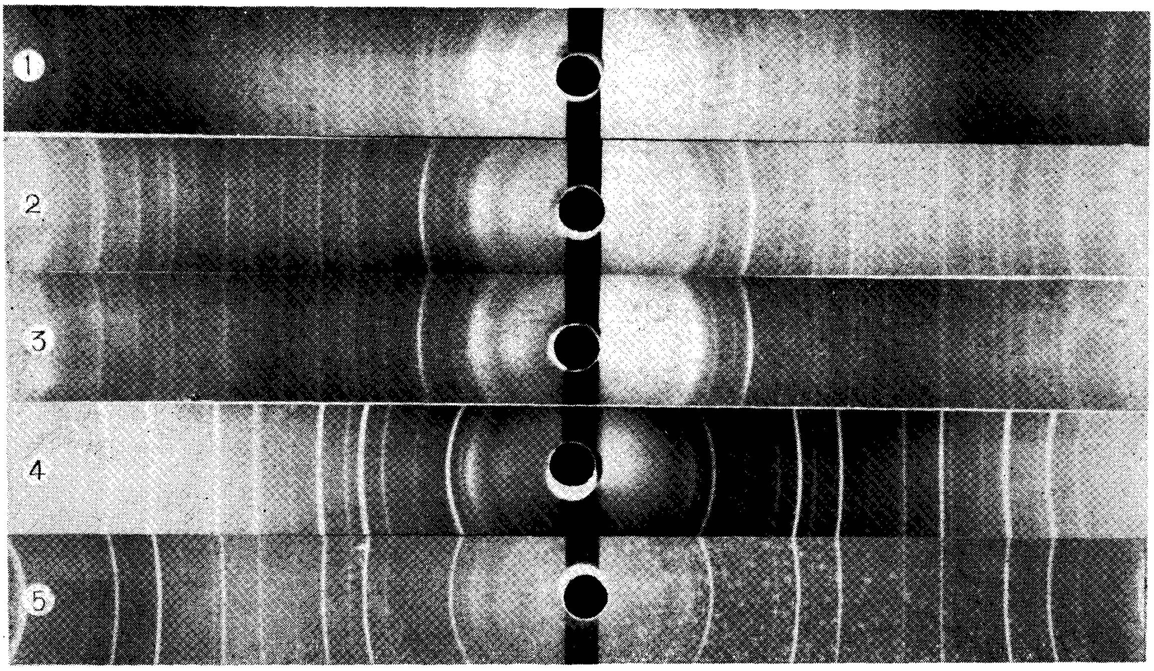
By the way, GeS_2 prepared in wet process had no such crystal structure.

2. Experimental results

GeS is known in literature as the lower sulfide produced by reduction of GeS_2 with hydrogen.(12) In order to ascertain the compound produced from GeS_2 by reduction, preliminary tests were carried out on its reduction with hydrogen for a few hours at 435°C. Then the color of the sample in the boat changed to greyish black and a black scaly compound recalling the appearance of iodine crystal was deposited on the inner wall of the reaction tube in the vicinity of the hole into the out-going gas tube. This agrees with the observation of Dennis et al.(13) and its X-ray diffraction pattern is given in Phot. 2. The lines in this photograph are in ageement with those of synthesized GeS (Phot. 3). Therefore it was inferred that the following reaction takes place:

$$GeS_2 + H_2 = GeS + H_2S.$$

The flow rates of hydrogen of 3.49, 5.58, 6.97 and 8.36 cc/min were used at each temperature of 390°, 415°, 435° and 485°C and the outgoing gases were analyzed to determine the values of $(H_2S)/(H_2)$ (ratio of the partial pressures).



X-ray diffraction patterns.
Diameter of camera: 60.50mm. With Fe K_α radiation.
Phot. 1. GeS_2 (Synthesized).
Phot. 2. GeS (Vaporized from GeS_2 in a stream of hydrogen).
Phot. 3. GeS (Synthesized).
Phot. 4. Ge (Reduced from GeS by hydrogen).
Phot. 5. Ge (Powder made in England).

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(12) J. W. Mellor, *A. Compr. Treat. Inorg. Theor. Chem.*, **VII** (1930), 273.

(13) L. M. Dennis and R. E. Hulse, J. Amer. Chem. Soc., **52** (1930), 3553.

Table 1. Observed values of equilibrium constants in hydrogen reduction of GeS_2 at selected temperatures and rates of flow. $((H_2S)/(H_2)\times 10^3)$.

Temperature	Rate of flow (cc/min)				
(°C)	8.36	6.97	5.58	3.49	0
390	1.22	1.69	1.82	2.98	4.05*
415	5.31	5.55	6.10	6.40	7.27*
435	6.62	7.09	8.11	9.22	11.1*
485	26.4	27.1	28.0	31.4	34.5*

* Extrapolated value.

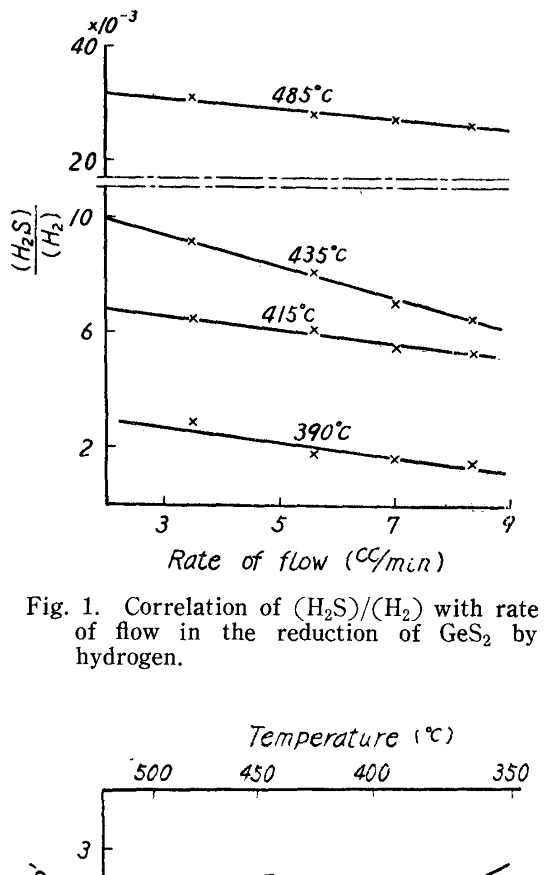

Fig. 1. Correlation of $(H_2S)/(H_2)$ with rate of flow in the reduction of GeS_2 by hydrogen.

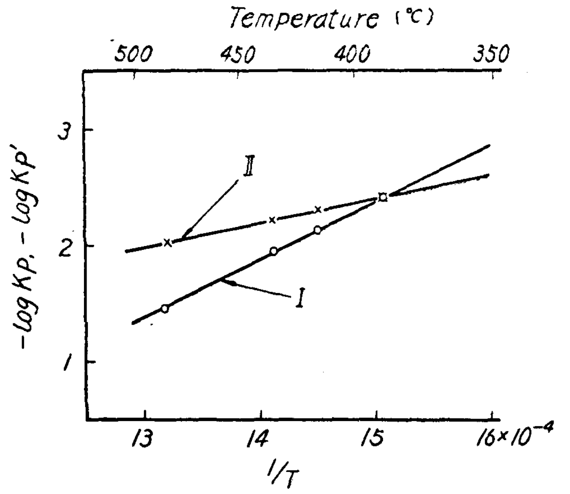

Fig. 2. Correlation of the equilibrium constants in hydrogen reduction of GeS_2 and GeS with temperature.

I. $GeS_2+H_2 = GeS+H_2S$, K_p.

II. $GeS + H_2 = Ge+H_2S$, K_p'.

The results obtained are summarized in Table 1. Employment of higher temperature than above seems to accompany violent vaporization of GeS to close the capillary of the out-going gas tube. Therefore the present authors carried no further experiment at higher temperatures. The observed values of $(H_2S)/(H_2)$, plotted against the flow rate, are shown in Fig. 1. From this figure the resultant points were known to lie on a straight line at each temperature. Therefore the values of $(H_2S)/(H_2)$ determined by extrapolating each line to zero flow rate were regarded to give the equilibrium constants in gas phase. The claculated values are given in the right end column of Table 1. The values of log K_p calculated from these data are given in Table 2. The temperature dependence of K_p is represented in Fig. 2, where log K_p is plotted against $1/T$, and a straight line is drawn through the experimental points. The equation of this straight line is expressed as follows:

$$\log K_p = -\frac{4876}{T} + 4.951. \quad (1)$$

The values of log K_p were calculated from above equation at each temperature of the present experiment. The results are given in the lowest line of Table 2. These are in good agreement with the observed ones.

Table 2. $GeS_2+H_2=GeS+H_2S$; $K_p=(H_2S)/(H_2)$.

Temperature (°C)		390	415	435	485
Absolute temperature (°K)		663	688	708	758
$1/T\times10^4$		15.08	14.53	14.12	13.19
$K_p\times10^3$		4.05	7.27	11.1	34.5
$-\log K_p$	(Observed)	2.398	2.138	1.955	1.462
	(Calculated)	2.402	2.134	1.934	1.480

Using this equation, the following one is obtained for representing the temperature dependence of the standard free energy change in this reaction.

$$\Delta F_1^\circ = 22303 - 22.65T. \qquad (2)$$

3. Dissociation pressure of GeS_2

Combining experimental equation (1) representing the temperature dependence of the equilibrium constant in the reduction of GeS_2 by hydrogen with that concerning the formation of H_2S gas, the next equation is deduced for illustrating the temperature dependence of the dissociation pressure of GeS_2:

$$2GeS_2 = 2GeS + S_2;$$

$$\log p_{S_2} = -\frac{19138}{T} + 15.002. \qquad (3)$$

The values of $\log p_{S_2}$ calculated from this equation at each experimental temperature are given in line (II) of Table 3.

Table 3. $2GeS_2 = 2GeS + S_2$.

Temperature (°C)		390	415	435	485
$-\log K_p$ (Observed)		2.398	2.138	1.955	1.462
$\log D_{H_2S}$ (Calculated)		8.865	8.375	8.010	7.177
$-\log p_{S_2}$	(I)	13.661	12.651	11.920	10.101
	(II)	13.858	12.805	12.021	10.241

Furthermore, the equation representing the temperature dependence of the standard free energy change in the dissociation of GeS_2 is derived from the above as follows:

$$\Delta F_2^\circ = 87540 - 68.62T. \qquad (4)$$

On the other hand, Schenck(14) has reported the exact equation concerning the temperature dependence of the equilibrium constant in the dissociation of H_2S gas. Using his equation, the values of $\log D_{H_2S}$ (D_{H_2S} represents the equilibrium constant in the dissociation of H_2S gas) were calculated at each temperature. The results are also given in Table 3. Combining these values with those of $\log K_p$ observed in this experiment, the values of $\log p_{S_2}$ were calculated, and the results are given in line (I) of Table 3. As shown in Table 3, there is a little discrepancy between these values. This arises from employing above simple equation, which was

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(14) H. Schenck, *Physik.-Chemie Eisenhuettenwesen*, I (1932), 265.

determined at higher temperature than the present one for expressing the temperature dependence of the equilibrium constant in the formation of H_2S gas, as already pointed out by one of the present authors.(15)

Exactly speaking, the values in line (I) of Table 3 should be employed. Looking at the values in this table, however, it may be recognized that simple equations (3) and (4) are employable over this temperature range.

When the values of $\log p_{S_2}$ are plotted against $1/T$, the points are fitted by a straight line as shown in line I of Fig. 3. From this figure, it is obvious that there is a linear correlation between them.

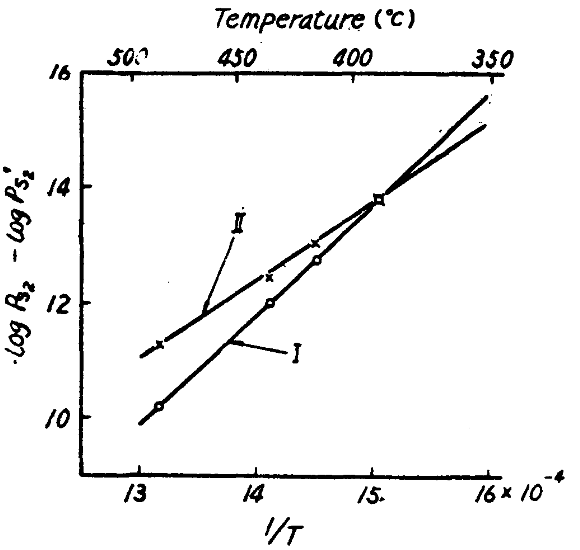

Fig. 3. Correlation of the dissociation pressures of GeS_2 and GeS with temperature.
I. $2GeS_2 = 2GeS + S_2$, $\log p_{S_2}$.
II. $2GeS = 2Ge + S_2$, $\log p'_{S_2}$.

IV. On the reduction of GeS with hydrogen

1. Material

The same dry synthetic process as in the case of GeS_2 was employed for its preparation. Considering the vaporizing property of GeS, such a preliminary treatment as above was avoided. The sulfur content of this compound was determined to be 31.03 per cent (theoretical value is 30.63 per cent). Fmploying the flow method as in this case, minor amounts of excess sulfur, if present, is removed as H_2S gas in the early period of experiment. Accordingly this material was used for the present measurement. Its X-ray diffrcation pattern is shown in Phot. 3. The lines coincide with those of GeS produced from GeS_2.

2. Experimental results

The equation representing the reduction of GeS with hydrogen is given as follows:

$$GeS + H_2 = Ge + H_2S\,.$$

In this case, it is thought that germanium hydrides are formed from the produced germanium and hydrogen gas.

The next three compounds are known as germanium hydrides.(16)

Hydride	GeH_4	Ge_2H_6	Ge_3H_8
Boiling point (°C)	−88.36	30.8	111.1

Upon considering above reaction, therefore, these compounds should not be neglected. These hydrides, however, are known to decompose at the temperatures from 340° to 360°C. This property is used to prepare thin germanium film which

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(15) K. Sudo, Bull. Res. Inst. Min. Dress. Met. (in Japanese), 8 (1952), 109.

(16) F. D. Rossini, D. D. Wagaman, W. H. Evans, S. Levine and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, (1947), 647.

is of important for electronic use.(2)

Phot. 4 is the X-ray diffraction pattern of the product obtained by keeping GeS in a stream of hydrogen gas with a flow rate of 6.97 cc/min at 435°C until the H_2S content in the out-going gas decreased to a small quantity.

The X-ray diffraction pattern of pure germanium is given in Phot. 5, which shows similar lines as above (Phot. 4).

Considering the facts, provided that the experiment is carried out at higher temperatures than above, the described equation, in which the formation of germanium hydrides is not taken into account, may be deemed sufficiently employable.

On the contrary, when the measuring is made at too high temperatures the amount of vaporized GeS increases so as to close the tube hole for the outgoing gas. Paying regard also to the rather low melting point of GeS itself, the ratio of $(H_2S)/(H_2)$ were measured for hydrogen flow rates of 3.49, 5.58, 6.97 and 8.36 cc/min at temperatures of 390°, 415°, 435° and 485°C. The results are summarized in Table 4. When the values of $(H_2S)/(H_2)$ were plotted against flow rate, the resultant points are fitted by a line at each temperature as seen in Fig. 4. Accordingly by extrapolating each line to zero rate of flow, the values of equilibrium constant K_p' were calculated and the results are given in the right end column of Table 4. To determine the correlation of $\log K_p'$ with temperature from above data, the values of $\log K_p'$ were calculated at each temperature. The results are plotted as $\log K_p'$ vs. $1/T$ in Fig. 2. As can be seen in this figure, the points are all fitted by a straight line given by the following expression :

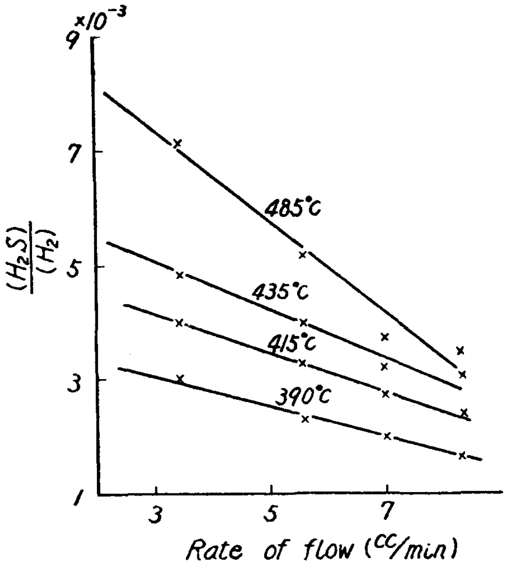

Fig. 4. Correlation of $(H_2S)/(H_2)$ with rate of flow in the reduction of GeS by hydrogen.

$$\log K_p' = -\frac{2113}{T} + 0.773. \qquad (5)$$

Table 4. Observed values of equilibrium constants in hydrogen reduction of GeS at selected temperatures and rates of flow. $((H_2S)/(H_2) \times 10^3)$

Temperature	Rate of flow (cc/min)				
(°C)	8.36	6.97	5.58	3.49	0
390	1.72	1.98	2.29	3.02	3.88*
415	2.40	2.71	3.32	3.98	5.04*
435	3.05	3.19	3.96	4.82	6.10*
485	3.53	3.74	5.20	7.12	9.73*

* Extrapolated value.

The values of $\log K_p'$ at each temperature calculated from above equation are given in Table 5. Since the values agree fairly well with the observed ones, the simple equation is considered to be sufficiently employable.

Table 5. $GeS + H_2 = Ge + H_2S$; $K_p' = (H_2S)/(H_2)$.

Temperature (℃)		390	415	435	485
Absolute temperature (°K)		663	688	708	758
$1/T \times 10^4$		15.08	14.53	14.12	13.19
$K_p \times 10^3$		3.88	5.04	6.10	9.73
$-\log K_p'$	(Observed)	2.411	2.298	2.215	2.012
	(Calculated)	2.413	2.297	2.211	2.014

Accordingly the temperature dependence of the standard free energy change of the reduction with hydrogen is represented as follows:

$$\Delta F_3^\circ = 9665 - 3.536T. \qquad (6)$$

3. Dissociation pressure of GeS

Combining above experimental equation (5) representing the temperature dependence of the equilibrium constant in the hydrogen reduction of GeS with that of the formation of H_2S gas, next simple equation was obtained for expressing the temperature dependence of dissociation pressure of GeS itself.

$$2GeS = 2Ge + S_2, \quad \log p_{S_2}' = -\frac{13612}{T} + 6.646. \qquad (7)$$

Using this equation the values of $\log p_{S_2}'$ were calculated at each experimental temperature and the results are given in Table 6.

Table 6. $2GeS = 2Ge + S_2$.

Temperature (℃)		390	415	435	485
$-\log K_p'$ (Observed)		2.411	2.298	2.215	2.012
$\log D_{H_2S}$ (Calculated)		8.865	8.375	8.010	7.177
$-\log p'_{S_2}$	(I)	13.687	12.971	12.440	11.201
	(II)	13.881	13.132	12.574	11.308

Furthermore the simple equation representing the temperature dependence of the standard free energy change in the dissociation of GeS is deduced from above one.

$$\Delta F_4^\circ = 62260 - 30.40T. \qquad (8)$$

Employing the exact equation reported by Schenck concerning the dissociation of H_2S gas, the dissociation pressures of GeS were calculated at each temperature as done in the case of GeS_2. The results are given in Table 6.

Since these agree fairly well with those deduced from the above simple equation, the simple equation is regarded to be sufficiently employable.

The results are plotted as $\log p_{S_2}'$ vs. $1/T$ in Fig. 3. The points are all fitted by straight line II. This figure obviously shows the linear relation between them.

V. Considerations regarding the smelting of sulfide ores containing germanium

From the experimental results above mentioned, the following fact can be easily known. The dissociation pressure of GeS_2 is higher than that of GeS at high temperatures and *vice versa*. The temperature where the dissociation pressures of both sulfides come to the same value was determined to be 388°C by use of experimental equations (3) and (7). That is, GeS is stable above 388°C and GeS_2 below this temperature.

On the other hand, GeO_2 is known to be more stable than GeO in the Ge-O system.

These facts are considered to satisfy the general rule described by Harner in a book edited by Hampel(17) : Germanium is both divalent and tetravalent, the latter compounds are the more stable.

These facts coincide with the description which gives GeS_2 as the germanium sulfide in natural minerals.

The temperature where the dissociation pressure of GeS_2 to GeS reaches 1 atm was determined to be 1,003°C by extrapolation of above experimental equation (3). That is, under normal pressure GeS_2 dissociates completely into GeS at about 1,000°C. Upon heating ores containing GeS_2 to this temperature, therefore, it must decompose into GeS and vaporize. Using this behaviour Kenworthy and Absalom(18) recovered germanium in zinc sulfide concentrate. Namely, they reported that the optimum recovery of germanium was obtained by heating the concentrate for 3 hours at 1,000°C in an atmosphere of He. In this case, for reducing the pressure in the reaction chamber volatilization must take place at lower temperatures than above. They also tested with respect to this point and obtained maximum volatilization of GeS in vacuo at 900°C.

Johnson et al.(19) volatilized out As_2S_3 by heating germanite in a stream of nitrogen at 800°C to concentrate germanium in it. This process is considered to be adequate from the fact that the equilibrium value of dissociation pressure of GeS_2 to GeS is calculated to be 1.5×10^{-3} atm at this temperature, As_2S_3 boils already at 707°C. Then their process for volatilization of GeS produced by heating GeS_2 thus obtained in a stream of ammonia at 825°C is of the same kind of reduction method with hydrogen as the present experiment. While the value of $(H_2S)/(H_2)$ under equilibrium state at this temperature calculated from the present experimental equation is 3.2, that of GeS to Ge is 7.2×10^{-2} and therefore the vaporization is considered to take place almost as GeS.

The germanium which stains the vaporized GeS is considered to be formed by secondary reactions as follows: Since the vapor pressure of germanium itself is

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(17) C. A. Hampel, *Rare Metals Handbook*, (1954), 165.

(18) H. Kenworthy and J. S. Absalom, U. S. Bur. Mines, Rept. Invest., No. **4876** (1952); C. A., **46** (1952), 6562.

(19) W. C. Johnson, L. S. Foster and C. A. Kraus, J. Amer. Chem., Soc., **57** (1935), 1828.

very low as deduced from the equation reported by Searcy(20) on liquid germanium, it comes from either the reduction of a part of gaseous GeS with hydrogen or the following direct decomposition of GeS:

From equations (4) and (8), next equation is obtained,

$$2GeS = GeS_2 + Ge; \quad \Delta F_5^\circ = -12640 + 19.11T. \qquad (9)$$

The sign of ΔF_5° calculated from above equation is positive at higher temperature than 388°C. That is, at higher temperatures where the vaporization of GeS takes place, the values of ΔF_5° have the positive sign, viz., the above reaction progresses to the left, at lower temperatures the sign turns negative, viz., the above reaction progresses to the right.

The above interpretation corresponds to the observation reported by Kimura et al.(21) upon inspecting the behaviour of germanium in copper arsenide consentrate from Obira Mine: Germanium is hardly removed at the stage of arsenic volatilization.

As can be deduced from above experiment III and X-ray Phot. 4 and 5, pure germanium can be produced directly from its sulfides by means of reduction with hydrogen. Because of the great dependency of the reaction velocity upon temperature, it may be thought desirable to hold the reaction temperature as high as possible in industry. On the other hand, the melting point of GeS is determined to be 625°C. Accordingly it seems to be unsuitable as a practical procedure for desulfurization to heat it up to higher temperatures than this. This may be a reason why the general procedure for preparation of pure germanium from its sulfides is the hydrogen reduction method of GeO_2 made by roasting the sulfides.

Summary

With a view to knowing the dissociation pressures of germanium sulfides, the equilibria in the reduction with hydrogen gas of germanic and germanous sulfides synthesized from the elements were measured by the flow method.

The experimental results obtained at selected temperatures from 390° to 485°C were found to be represented by the equations:

$$GeS_2 + H_2 = GeS + H_2S; \qquad K_p = (H_2S)/(H_2),$$

$$\log K_p = -\frac{4876}{T} + 4.951,$$

$$\Delta F_1^\circ = 22303 - 22.65T.$$

$$GeS + H_2 = Ge + H_2S; \qquad K_p' = (H_2S)/(H_2),$$

$$\log K_p' = -\frac{2113}{T} + 0.773,$$

$$\Delta F_3^\circ = 9665 - 3.536T.$$

Combining these equations with the known ones for hydrogen sulfide gas, the

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(20) A.W. Searcy, J. Amer. Chem. Soc., **74** (1952), 4789.

(21) K. Kimura, S. Kano, K. Saito and N. Tatara, J. Chem. Soc. Japan (in Japanese), **73** (1952), 677.

dissociation pressures and the standard free energy changes in the dissociation of solid germanium sulfides were given as a function of temperature by the following equations :

$$2GeS_2 = 2GeS + S_2 ;$$

$$\log p_{S_2} = -\frac{19138}{T} + 15.002,$$

$$\Delta F_2^\circ = 87540 - 68.62T.$$

$$2GeS = 2Ge + S_2 ;$$

$$\log p_{S_2}' = -\frac{13612}{T} + 6.646,$$

$$\Delta F_4^\circ = 62260 - 30.40T.$$

Basing themselves on these data, the behaviour of germanium in the process of smelting of sulfide ores was discussed.

Acknowledgement

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