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<th>著者</th>
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Vapor Pressure of Lead and Germanium Sulphides

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Synopsis

As a part of fundamental researches in distillation process, the vapor pressure of lead and germanium sulphides was measured in the range 775° to 920°C and 433° to 596°C respectively by using the Knudsen method. From the results obtained, the following experimental formulae were derived for representing the relation between the vapor pressure and temperature:

\[
\begin{align*}
\text{PbS(s)} &= \text{PbS(g)}, & \log p_{\text{atm}} &= -\frac{11780}{T} + 7.448, \\
\text{GeS(s)} &= \text{GeS(g)}, & \log p_{\text{atm}} &= -\frac{6966}{T} + 6.215.
\end{align*}
\]

By using the above data and other thermodynamic values of metallic sulphides, a brief discussion was made on their behaviour in the processes of reducing smelting.

I. Introduction

For the purpose of completely recovering all valuable minerals in ores, there are few cases in recent smelting technology, where behaviour of metals or their compounds at various metallurgical processes is used for separating one from other. It is well known that in processes of non-ferrous metals smelting or refining, in particular, many cases make use of volatilities of objective metals or their compounds. During the World War II researches in the uses of atomic energy and in others resulted in a remarkable advance in vacuum technology. Also rare metals which had been hardly used before were found to be useful as materials for electronics and reactors. Since then various methods based on their vaporization or compounds have been widely employed as their refining methods. On the other hand, these volatilities are important problems in vacuum melting which is recently considered to be a hope for the removal of volatile impurities, or as a method of adding various alloying elements.

The present author has continued to make fundamental researches on smelting of sulphide ores which is considered to be a principal process of non-ferrous extraction metallurgy. When the flow method is used for measuring dissociation pressures of various metallic sulphides, the present author observed that some metallic sulphides show high vapor pressure, which he intended to measure in order to supply data for studying processes in metallurgical smelting. The present author measured vapor pressure of lead and germanium sulphides which had shown

high pressures in his previous experiments, and reported in the present paper.

II. Method of measurement and apparatus

There have been many proposals for measuring vapor pressure and they are classified into the following three groups whose characteristics, etc, have been already described elsewhere. The compilation of measured values of various metals and their compounds are also found in the papers of Kelley,(1) Stull(2) and Kubaschewski et al(3).

(1) Direct method. (2) Indirect method.

(3) Method based on kinetic theory of gas.

The present author employed one in the third group because of its high accuracy. When employing this method, a special container limits its applicability to compounds. So far as PbS and GeS were concerned, fortunately this method could be employed in the present experiment.

The effusion method was proposed by Knudsen(4) in 1909 and since then has been used for measuring vapor pressure of various solid salts. This is based on the rate at which a gas escapes through a small orifice into a vacuum. The following relation holds:

\[ p = \frac{m}{tA} \sqrt{\frac{2\pi RT}{M}} = 0.02256 \frac{m}{tA} \sqrt{\frac{T}{M}}, \]

where \( p \) is the pressure of the objective substance (atm), \( m \) the mass of gas of molecular weight \( M \) passing through an orifice of area \( A \) (cm\(^2\)) in time \( t \) (sec), \( R \) the gas constant and \( T \) the absolute temperature.

Fig. 1 shows the apparatus used in this experiment. Dimensions of the container, main part of the apparatus, are given in Fig. 2, which is the same as that used by Shibata and Niwa(5) for measuring the vapor pressure of solid

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mercubic chloride. This consists of a couple of ground jointed silica cups, the upper center part of which is very thin and has a very small hole (although the hole plate is desirable to have an infinitely small thickness, a real hole forms a microscopic tube, and therefore, exact correction on this point must be taken into account. Fortunately, in the present experiment this thickness was so small that no correction was needed). Three hooks for hanging the vessel are provided on the outer side of the lower cup. The joint was made extremely careful about its grinding to prevent any loss of the vapor through the clearance, because, contrary to usual vacuum cocks, no grease can be used in this joint. The container in which the sample was placed was hung from the silica thermobalance with a small platinum or silica rod, as shown in Fig. 1. Weight change was known by observing the position of a cross on a small mirror attached to the spring with a travelling microscope. After setting the container in a given position, a silica reaction tube (6) was set in the bottom, and while leading cooling water into the water jacket in order to prevent fusion of the grease on the ground joint part, the inner part was evacuated with a rotary vacuum pump and a mercury diffusion pump, and the air tightness was tested. The trap (10) was cooled with a thermos containing a freezing mixture of solid carbonic acid and ethyl alcohol. An electric furnace kept at a given temperature was quickly brought up to the above reaction tube and a Pt-Pt-Rh thermocouple was inserted in a silica tube which was placed in a hole of the reaction tube just under the container. The heating element of the furnace was elema and a porcelain tube was placed insides of the furnace for the purpose of uniform heating. When heating the tube, an asbestos ring was placed at the mouth of the furnace to prevent radiation. After bringing up the furnace, the temperature of the insides of the reaction tube reached the furnace temperature and thereafter change in weight was measured by a microscope at constant intervals. The results were plotted on a section paper to determine the vaporization rate. Though the trap (10) was to prevent any vaporized material from entering the vacuum pump, no deposition reached this trap under the present experimental conditions and this was probably due to perfect cooling by water. Nearly all of them were deposited on the upper part of the silica reaction tube and after continuing the experiment for a long time cloudiness was observed on the inner wall of the sphere part (9). A correction upon deposition of vaporized materials on the hanging rod should be taken into consideration and however the amount was negligible in this experiment. In the experiment on lead sulphide

the platinum wire was attacked and sometimes broken off during the measurement and thereafter fine silica rods were used.

The area of the hole on the sample container was first measured with a planimeter after enlarging under a microscope. However, this operation was troublesome and in most cases determination of the area could be done from the average values of the diameter measured in every direction about ten times, because each formed a nearly perfect circle. Therefore the direct method was generally employed except for small ones and especially for examining a change in diameter after experiment. The silica spiral springs were made in the glass works of the institute and had sensitivities of 0.476 to 0.488 mg/reading.

### III. Vapor pressure of lead sulphide

Schenck and Albers\(^7\) measured it at relatively higher temperature by sending purified nitrogen gas on lead sulphide to prevent its oxidaton. Basing on their results, except two values which seemed to be erroneous, Kelley calculated a formula representing the temperature dependence of the vapor pressure. Veselovskii\(^8\) used the same Knudsen method as that used in this experiment and obtained nearly the same entropy value of PbS\((g)\) as the known one, \(S^{0}_{\text{298.1}} = 60.13\). On the other hand, Hsiao and Schlechten\(^9\) measured by the Langmuir method at rather lower temperature and obtained a formula representing the correlation of the vapor pressure with temperature which fairly differed from Kellleys one. From the above data Kubaschewski and Evans\(^3\) proposed another formula which coincided with Kellleys one.

1. **Sample**

   Samples were prepared by a wet method and refined by a dry process. They were the same as those used for measuring their dissociation pressure in the previous experiment\(^10\). They contained the theoretical amount of sulphur. Their high purity was expected from their fine crystalline appearance after the experiment. Approximately 0.5 g of the sample was used every time.

2. **Results and discussion**

   The experimental conditions and the results obtained are given in Table 1. The container having the hole area of \(2.69 \times 10^{-4} \text{ cm}^2\) was used many times, because of its good make and circular hole. After each experiment the hole was examined under a microscope, and when needed this was cleaned with acid and dried and then used for next experiment.

   From the results the relation between \(\log p\) and \(1/T\) is shown in Fig. 3, in which the points obtained are fitted by a straight line. This experimental formula is as follows:

\(^7\) R. Schenck and A. Albers, Z. anorg. Chem., 105 (1919), 145.
Table 1. Experimental results of measurement on PbS.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>1/T x 10^4</th>
<th>Area of hole x 10^4 (cm²)</th>
<th>Rate of vaporization x 10^6 (g/sec)</th>
<th>log P (atm)</th>
<th>log p (mm Hg)</th>
<th>Remarks</th>
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<td>920</td>
<td>8.38</td>
<td>9.54</td>
<td>19.0</td>
<td>-2.4488</td>
<td>+0.4320</td>
<td>mean</td>
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<tr>
<td>920</td>
<td>8.38</td>
<td>2.69</td>
<td>32.5</td>
<td>-2.3976</td>
<td>+0.4832</td>
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<td>32.0</td>
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<td>+0.4764</td>
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<tr>
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<td>6.09</td>
<td>19.4</td>
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<td>+0.4410</td>
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<td>872</td>
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<td>7.73</td>
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</tr>
<tr>
<td>775</td>
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<td>40.9</td>
<td>1.46</td>
<td>-3.7732</td>
<td>-0.8924</td>
<td></td>
</tr>
</tbody>
</table>

\[
PbS(s) = PbS(g), \quad \log P_{(atm)} = -\frac{11780}{T} + 7.448,
\]

\[
\Delta F^o = 53880 - 34.07T.
\]

In the figure, other measured values and a line calculated by Kelley are also shown. The present results are higher than those of Hsiao et al. and a bit lower than those of Kelley. The values obtained by Schenck et al. from which Kelley derived his formula are those in the higher range of vapor pressure, those of Hsiao et al. in the lower range and the present data in the middle.

Basing the present data and thermodynamical values of Kelley\(^{(11)}\) (though the value of specific heat of PbS(s) given by Kubaschewski et al. differs a little from Kelleys value, it has little effect on the result), the following formulae were calculated to represent the correlation of \(\Delta H\) and \(\Delta F^o\) with temperature:

\[
PbS(s) = PbS(g), \quad \Delta H = 58290 - 1.63T - 2.00 \times 10^{-3}T^2,
\]

\[
\Delta F^o = 58290 + 37.5T \log T + 2.00 \times 10^{-3}T^2 - 51.70T,
\]

\[
\Delta H_{298.1} = 57630, \quad (60216),
\]
\[ \Delta F^{\circ}_{298.1} = 45820, \quad (47542). \]

The entropy of PbS(s) is given as follows\(^{(11)}\): PbS(s), \(S^0_{298.1} = 21.8\), therefore, the entropy values of PbS(g) is as follows: PbS(g), \(S^0_{298.1} = 61.4\), (64.3), where the values in the parenthesis on the right side are those of kelley or the ones calculated from his data.

On the other hand, other entropy value of PbS(g) is given by other method to be 60.18. This fairly agrees with the present one. Then the present data are considered to have high reliability and agree with the results obtained by Veselovskii.

IV. Vapor pressure of germanium sulphide

High volatility of GeS was reported in the previous paper by the present author et al\(^{(12)}\), and the measurement was recently made by Kenworthy et al\(^{(13)}\), by means of the flow method and the results were reported.

1. Sample

Samples were prepared by the dry method the same as that used for measuring the dissociation pressure by the present author et al.

2. Results and discussion

The experimental conditions and the results obtained are given in Table 2.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>(\frac{1}{T} \times 10^4)</th>
<th>Area of hole (\times 10^4) (cm(^2))</th>
<th>Rate of vaporization (\times 10^6) (g/sec)</th>
<th>(\log p) (atm)</th>
<th>(\log p) (mm Hg)</th>
</tr>
</thead>
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<tr>
<td>596</td>
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<td>11.01</td>
<td>231</td>
<td>-1.8562</td>
<td>+1.0156</td>
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<tr>
<td>535</td>
<td>12.38</td>
<td>11.01</td>
<td>85.7</td>
<td>-2.3116</td>
<td>+0.5692</td>
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<tr>
<td>487</td>
<td>13.16</td>
<td>11.01</td>
<td>19.7</td>
<td>-2.9634</td>
<td>-0.0826</td>
</tr>
<tr>
<td>433</td>
<td>14.16</td>
<td>85.71</td>
<td>3.97</td>
<td>-3.6751</td>
<td>-0.7943</td>
</tr>
</tbody>
</table>

Experiments were carried out twice at each temperature with the same container of good shape. The results obtained agree with each other at each temperature and therefore only the average values are given. The results are plotted in Fig. 4, which shows a linear relation between \(\log p\) and \(1/T\). The relation is represented by the following formulae:

\[
\text{GeS(s)} = \text{GeS(g)}, \quad \log p_{(\text{atm})} = - \frac{6966}{T} + 6.215,
\]

\[
\Delta F^{\circ} = -31860 - 28.43T.
\]

The results of Kenworthy et al. are also given in the figure and they are higher than the present ones. Though discussions can't be made accurately on their


results for lack of detailed report on their experimental conditions, the following two reasons for this discrepancy are conceivable.

When using a flow method, optimum flow rate must be selected, otherwise, true equilibrium values are not always obtained by extrapolating the flow rate to zero. That is, when employing too high flow rate, most of the outgoing gas passes over the sample without any reaction. On the contrary, when employing too low flow rate, the relation between the composition of outgoing gas and the flow rate shows an curve and then extrapolation can hardly be done. The latter seemed to be the case with the results of Kenworthy et al. and their description of great dissociation of GeS at about 600°C was thought to be abnormal from the results in the previous report of the present author et al.\(^1\)\(^2\) Basing on the X-ray study of the present author et al., rather a long time was required to crystallize synthetic GeS and therefore the sample of Kenworthy et al. was thought to be the result of incomplete crystallization.

V. Discussion on behaviour of metallic sulphides during smelting processes

Though smelting practices of sulphide ores consist of various processes, only phenomena in reducing smelting are discussed in the present article. The vapor pressure of typical metallic sulphides in this process is shown in Fig. 5. The data on other sulphides than PbS and GeS come from the book of Kubeschewski et al.\(^3\) From this figure, GeS is seen to give a great tendency of volatilization and this may be regarded as a corroborative fact for interpretation by the present
author of the concentration process of germanium in copper smelting. The fact that PbS has also rather a strong tendency to vaporize is made use of in delead-
ing by Waelz process at Oker Smelter,(14) where lead is removed as PbS vapor at 1000°C after reducing PbSO₄ in zinc oxide to PbS at 900°C.

Considering recent development of atmospheric control, especially of fluosolid
furnace, and also of vacuum technique, such separation of metallic sulphides as
was proposed by Schlechten(15) seems to be effective from this figure.

Summary

By employing the Knudsen method, measurements of the vapor pressure were
made with lead and germanium sulphides synthesized in the laboratory. The
results obtained led to the experimental formulae as follows:

\[ \log p_{(\text{atm})} = -\frac{11780}{T} + 7.448, \]

\[ \Delta F^0 = 53880 - 34.07T. \]

\[ \log p_{(\text{atm})} = -\frac{6966}{T} + 6.215, \]

\[ \Delta F^0 = 31860 - 28.43T. \]

Based on these and known data on other metallic sulphides, a brief discussion was
made on the behaviour in the process of reducing smelting.

This study was made as a part of fundamental research in distillation process.
The author wishes to thank Director K. Ono and Professor M. Watanabe for their
encouragement.

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(15) A. W. Schlechten, E. M. J., 155 (1954), No. 11, 81.