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# Vapor Pressure Measurements of AgBr by the Knudsen Effusion Method

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## Abstract

The vapor pressure of silver bromide (AgBr) liquid was measured by the Knudsen effusion method. The ratio of the vapor species of silver bromide was calculated from the literature [3, 6], and the vapor pressures were calculated on the basis of the ratio. As reported in the literature [3], we considered the vapor species to be monomers (AgBr) and trimers (Ag<sub>3</sub>Br<sub>3</sub>). The partial pressures of AgBr [ $p_{\text{monomer}}$ (Pa)] and Ag<sub>3</sub>Br<sub>3</sub> [ $p_{\text{trimer}}$ (Pa)] were respectively fitted by the following linear equations over the temperature range 829.9–929.9 K:

$$\ln(p_{\text{monomer}}) = -(23590 \pm 519) / T + (25.22 \pm 0.59),$$

$$\ln(p_{\text{trimer}}) = -(19449 \pm 509) / T + (20.42 \pm 0.58).$$

The total vapor pressure of silver bromide [ $p_{\text{total}}$ (Pa)] fitted the following linear equation:

$$\ln(p_{\text{total}}) = -(21653 \pm 529) / T + (23.72 \pm 0.60).$$

Keywords: vapor pressure, silver bromide, Knudsen effusion method, vapor species

## 1. Introduction

Valuable metals contained in electrical/electronic waste can be vaporized and distributed into dust as metal bromides during incineration owing to bromine-containing flame retardants used in printed circuit boards and plastic parts. To manage these evaporation reactions, reliable vapor pressure data are needed. However, to date little research on the vapor pressure of metal bromides has been reported.

Silver is a precious metal, which has a remarkably low electrical resistance and is industrially important. However, only three reports of the vapor pressure values of silver bromide (AgBr) in the liquid state are available [1,2,3].

In 1929, Jellinek and Rudat [1] measured the vapor pressure of several metal halides using a transpiration apparatus devised by Jellinek and Rosner [4]. Jellinek and Rudat made three vapor pressure measurements of AgBr at 1273, 1373 and 1473 K.

In 1935, Kelly [5] collected literature on vapor pressure measurements of inorganic substances, and edited thermochemical properties calculated from the literature data. For silver bromide, only the data of Jellinek and Rudat were available, and Kelly mentioned that these data were insufficient to calculate the free-energy and gave an approximate vapor pressure equation.

In 1958, Bloom et al. [2] measured vapor pressures of AgBr at 15 different points from a temperature range of 1240–1497 K based on the boiling point method and reported a vapor pressure equation and boiling point for AgBr. In this method, the regent was inserted into a heat-resistant glass tube and heated in an electrical furnace. The inner pressure and the inner temperature of the furnace were controlled, and the vapor pressures were obtained from the boiling behavior of the regent. The boiling point of AgBr has been determined to be 1778±5 K in the literature; however, the value calculated by FactSage (version 6.4, Thermfact Ltd., Quebec, Canada, and GTT-Technologies, Herzogenrath, Germany) is 1833 K. This considerable difference might suggest that some other error factors are associated with the

previously reported experimental apparatus and/or the purity of the reagents.

The two trend lines of the vapor pressure equations in the high temperature range from reports of Bloom et al. [2] and Kelly [5] are somewhat close. The vapor pressure measurements of Jellinek et al. [1] and Bloom et al. [2] were reported more than 60 years ago.

In 2005, Hildenbrand and Lau [3] measured the vapor pressure of AgBr over the range of 805–936 K using the torsion-effusion method, and also estimated the vapor species of AgBr at 840 K. They reported that the principal vapor species were the monomer (AgBr) and the trimer (Ag<sub>3</sub>Br<sub>3</sub>). In the low temperature range, only the report from Hildenbrand et al. is currently available.

In this study, the vapor pressure of silver bromide was measured by the Knudsen effusion method in the low temperature range, and the partial pressures of the monomer and the trimer were calculated from the data of the Gibbs energy functions of previous studies [3,6].

## 2. Experimental details

### 2.1. Materials

The reagent AgBr (99.8%, Wako Pure Chemical Industries Ltd., Osaka, Japan) was used in the study. NaCl (99.9999%, Wako Pure Chemical Industries Ltd., Osaka, Japan) was used as a vapor pressure reference material. NaCl was melted under an argon atmosphere (99.9999%) and maintained under an argon flow for more than 1 h before the vapor pressure measurements to remove impurities. **Table 1** summarizes the information of the samples used in this study.

### 2.2. Knudsen effusion method

#### 2.2.1. Weight decrease measurement of Knudsen cells

The Knudsen effusion method was applied to measure the vapor pressures of AgBr [7]. The Knudsen cells were made of platinum. A single cell consisted of a body and a lid, and each cell lid had a hole (diameter: 0.16 mm). A cross-sectional view of the Knudsen cell is shown in **Fig. 1** [8]. Because platinum is known to form alloys with other metals at high temperatures, the amount of residue in the cells after the experiment was weighed to ensure that the silver in the reagent had not combined with platinum. The amounts of residue were as little as 0.9–2.1 wt% of the AgBr introduced into the Knudsen cell.

Sample powder placed at the bottom of the cell body was homogeneously pressed with a stainless-steel rod under an argon atmosphere. Then the cell lid was welded and pressed on the cell body to ensure that the Knudsen cell airtight. The Knudsen cell was then introduced into a thermal gravimetric analyzer (TGA, Thermo plus TG8120, Rigaku Corp., Akishima, Japan), with an inner pressure of approximately  $2.5 \times 10^{-4}$  Pa, and a heating rate of 10 K/min. The temperature of the Knudsen cell was measured with a thermocouple fitted in the TGA.

#### 2.2.2. Calculation of vapor pressures

Hildenbrand et al. [3] reported the Gibbs energy functions (gef) of AgBr gas and Ag<sub>3</sub>Br<sub>3</sub> gas, and Pankratz [6] reported the gef of AgBr liquid. The ratios of AgBr [ $x$  (-)] and Ag<sub>3</sub>Br<sub>3</sub> [ $1-x$  (-)] at six temperature points from 700–1200 K could be calculated from the equation  $\Delta\text{gef} = -\Delta(G_T^0 - H_{298}^0)/T$ , where  $G_T^0$  (J · mol<sup>-1</sup>) is the Gibbs energy and  $H_{298}^0$  (J · mol<sup>-1</sup>) is the standard enthalpy of formation. Hildenbrand et al. reported that  $H_{298}^0 = 12.4 \pm 0.1$  kJ for the evaporation of monomer [AgBr<sub>(l)</sub> = AgBr<sub>(g)</sub>], and  $H_{298}^0 = 12.7 \pm 0.12$  kJ for the evaporation of trimer [3AgBr<sub>(l)</sub> = Ag<sub>3</sub>Br<sub>3(g)</sub>]. An approximate polynomial:

$$x = -6 \times 10^{-8}T^3 + 5 \times 10^{-5}T^2 + 0.1814T - 102.92 \quad (700\text{-}1200 \text{ K}) \quad (1)$$

was calculated from the ratios of vapor species. The ratios at each measured temperature were decided from the

polynomial.

The Clausing factor of the cell depends on the geometry of the hole. The Clausing factor gives the probability of a molecule passing through a cylindrically shaped tubular hole, and is calculated by the following equation [9]:

$$K = 1/(1 + 0.5(L_0/r_0)), \quad (2)$$

where  $K$  (–) is the Clausing factor of the orifice,  $L_0$  (m) is the orifice length and  $r_0$  (m) is the orifice radius. The orifice area of the cell [ $A_0$  (m<sup>2</sup>)] was analyzed from a stereoscopic microscope image, and the equivalent radius of the area was decided by considering the orifice to be a circle. The heat expansion of the orifice was also considered by applying the linear expansion coefficient at each temperature to the radius. The vapor pressure data of NaCl, a reference substance, was obtained from FactSage (version 6.4, Thermfact Ltd., Quebec, Canada, and GTT-Technologies, Herzogenrath, Germany) and used to calibrate and define an apparatus constant [ $C$  (–)] of the experimental setup for the vapor pressure measurement. The calibration temperature range was 860–1000 K, and state of NaCl in the range is solid. The vapor pressure was calculated from the following equation:

$$p = \frac{\Delta W}{t} \cdot C \cdot \frac{1}{KA_0} \sqrt{\frac{2\pi RT}{M}} \quad (3)$$

where  $\Delta W/t$  (kg·s<sup>–1</sup>) is the weight decline speed of the cell,  $M$  (kg·mol<sup>–1</sup>) is molecular weight,  $R$  (J·mol<sup>–1</sup>·K<sup>–1</sup>) is the ideal gas constant, and  $T$  (K) is temperature. From **Eq. (3)**, the partial pressures should be:

$$p_{\text{monomer}} = \frac{\Delta W_{\text{monomer}}}{t} \cdot \frac{C}{KA_0} \sqrt{\frac{2\pi RT}{M_{\text{monomer}}}} \quad (4)$$

$$p_{\text{trimer}} = \frac{\Delta W_{\text{trimer}}}{t} \cdot \frac{C}{KA_0} \sqrt{\frac{2\pi RT}{M_{\text{trimer}}}} \quad (5)$$

where  $\Delta W_{\text{monomer}}/t$  (kg·s<sup>–1</sup>) and  $\Delta W_{\text{trimer}}/t$  (kg·s<sup>–1</sup>) are the partial weight decreases for the monomer and trimer, respectively. In the experiment, the total weight decrease  $\Delta W_{\text{total}}/t = \Delta W_{\text{monomer}}/t + \Delta W_{\text{trimer}}/t$  was obtained. The molecular weight of the monomer [ $M_{\text{monomer}}$  (kg·mol<sup>–1</sup>)] and trimer [ $M_{\text{trimer}}$  (kg·mol<sup>–1</sup>)] are simply related as  $3M_{\text{monomer}} = M_{\text{trimer}}$ . Partial pressures are indicated with total pressure [ $p_{\text{total}}$  (Pa)] and monomer ratio [ $x$  (–)] that  $p_{\text{monomer}} = x \cdot p$  and  $p_{\text{trimer}} = (1 - x) \cdot p$ . From these relations, **Eq. (6, 7)** are finally given as:

$$p_{\text{monomer}} = \frac{\Delta W_{\text{total}}}{t} \cdot \frac{C}{KA_0} \sqrt{\frac{2\pi RT}{M_{\text{monomer}}}} \cdot \frac{x}{x + \sqrt{3}(1-x)} \quad (6)$$

$$p_{\text{trimer}} = \frac{\Delta W_{\text{total}}}{t} \cdot \frac{C}{KA_0} \sqrt{\frac{2\pi RT}{M_{\text{monomer}}}} \cdot \frac{1-x}{x + \sqrt{3}(1-x)} \quad (7)$$

A linear least squares curve-fitting routine was applied to the obtained vapor pressure values, and the  $A$  (K) and  $B$  (–) constants in the following vapor pressure equation:

$$\ln(p) = -\frac{A}{T} + B, \quad (8)$$

were determined for  $p_{\text{monomer}}$  (Pa),  $p_{\text{trimer}}$  (Pa) and  $p_{\text{total}}$  (Pa), respectively.

### 3. Results and discussion

The vapor pressure values obtained for AgBr are shown in **Table 2**. The relative standard uncertainty (0.68 level of confidence) of the measured temperature was less than 0.0012% and that of pressure was less than 11.1%. Note that the

apparatus constant [ $C$  (-)] obtained from calibration by NaCl vapor pressure was in the range from 0.59–0.71. The constants  $A$  (K) and  $B$  (-) in **Eq. (8)** were derived from data of measurements by a linear least squares curve-fitting routine for the linear correlation between  $\ln[p$  (Pa)] and  $1/[T$  (K)]. The vapor pressure of silver bromide fitted the following linear equation over the temperature range of 829.9–929.9 K:

$$\ln(p_{\text{monomer}}) = -(23590 \pm 519) / T + (25.22 \pm 0.59) \quad (9)$$

$$\ln(p_{\text{trimer}}) = -(19449 \pm 509) / T + (20.42 \pm 0.58) \quad (10)$$

$$\ln(p_{\text{total}}) = -(21653 \pm 529) / T + (23.72 \pm 0.60). \quad (11)$$

**Table 3** summarizes the temperature dependence of the vapor pressures and evaporation enthalpy and entropy obtained in this study and those reported in the literature for silver bromide.

**Fig. 2** and **Fig. 3** show a comparison between the vapor pressures of AgBr obtained in this study and previous studies [1, 2, 3, 5]. The values from our study, those of Bloom et al., and those of Hildenbrand et al. were in line based on the vapor pressure equations. Values from Jellinek and Rudat are shown using three dots and the extrapolated values were in line with Kelly's equation. In the low temperature range, the trend line of this study was close to that of Hildenbrand et al., and was located between the two extrapolated values of previous studies in the high temperature range. In the high temperature range, the extrapolated values of our study were somewhat close to the values of previous studies. In the extrapolation, it was assumed that vapor species were all monomers in the high temperature range. These comparisons show that our measured vapor pressure values are located in a similar range to previously reported data. Additional measurements by other researchers might be expected to further improve the reliability of the vapor pressure values of AgBr.

#### 4. Conclusions

The vapor pressure of the silver bromide liquid was measured by the Knudsen effusion method. The ratios of monomer (AgBr) and trimer (Ag<sub>3</sub>Br<sub>3</sub>) were calculated from the previous literature data. The vapor pressures were fitted to linear equations over the temperature range considered.

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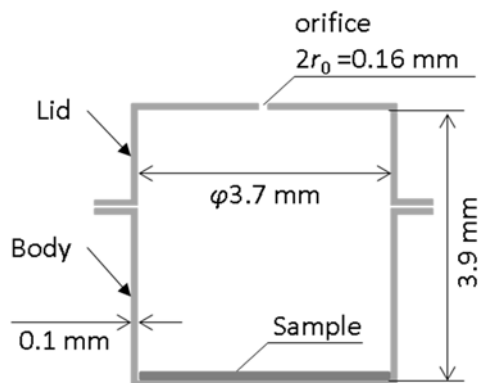
#### Notes

The authors declare no competing financial interests.

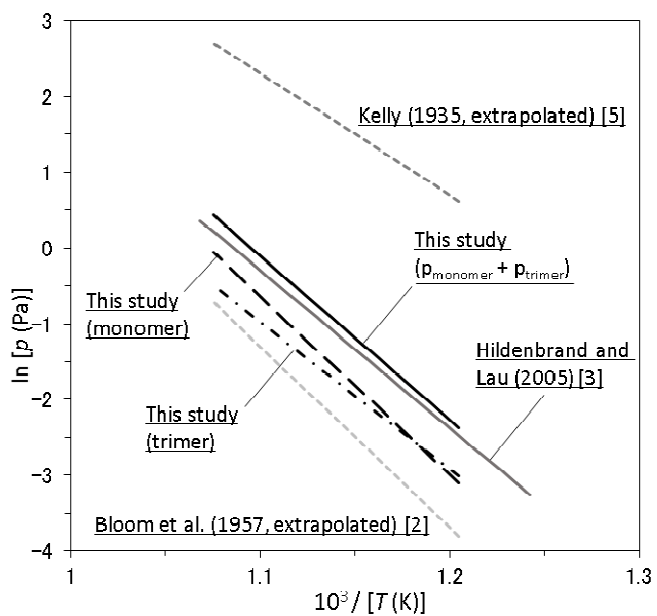
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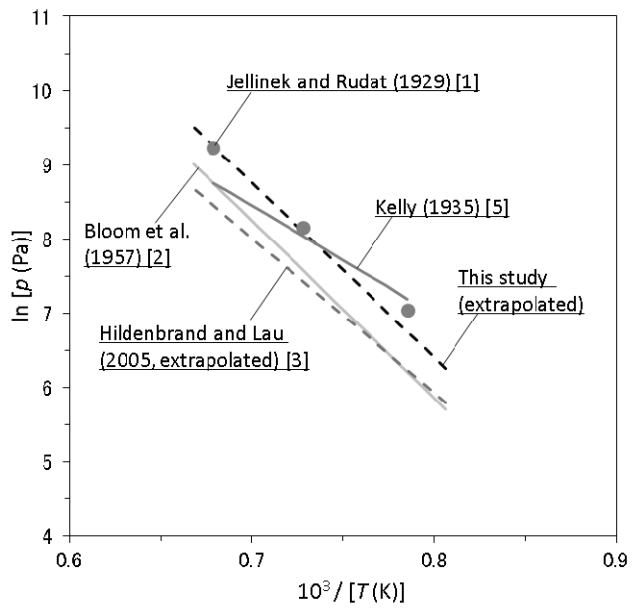
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**Fig. 1** Cross-sectional diagram of the Knudsen cell [7] (partly revised)



**Fig. 2** Comparison between values in this study and previous reports (lower temperature)



**Fig. 3** Comparison between values in this study and previous reports (higher temperature)



**Table 1** Vapor pressure data of this study

<b>Chemical Name</b>	<b>Source</b>	<b>Initial Purity</b>	<b>Purification Method</b>
AgBr	Wako Pure Chemical Industries Ltd.	99.8%	none
NaCl	Wako Pure Chemical Industries Ltd.	99.9999%	melted under an argon atmosphere and maintained under an argon flow for more than 1 h

**Table 2** Vapor pressure data of AgBr monomer and trimer over AgBr liquid obtained in this study

Run 1			Run 2		
$T$ (K)	$p_{\text{monomer}}$ (Pa)	$p_{\text{trimer}}$ (Pa)	$T$ (K)	$p_{\text{monomer}}$ (Pa)	$p_{\text{trimer}}$ (Pa)
829.9	0.041	0.045	829.9	0.052	0.057
849.9	0.075	0.073	849.9	0.096	0.094
869.9	0.145	0.127	869.9	0.168	0.148
890.0	0.336	0.266	889.9	0.295	0.234
910.0	0.667	0.476	909.9	0.499	0.356
929.9	1.214	0.784	929.9	0.845	0.546
Run 3			Run 4		
$T$ (K)	$p_{\text{monomer}}$ (Pa)	$p_{\text{trimer}}$ (Pa)	$T$ (K)	$p_{\text{monomer}}$ (Pa)	$p_{\text{trimer}}$ (Pa)
829.9	0.053	0.058	829.9	0.038	0.042
849.9	0.093	0.091	849.9	0.086	0.085
869.9	0.173	0.152	869.9	0.147	0.129
889.9	0.318	0.252	889.9	0.259	0.205
909.9	0.559	0.399	909.9	0.491	0.351
929.9	1.040	0.672	929.9	0.736	0.475

- i)  $T$  (K) is temperature,  $p_{\text{monomer}}$  (Pa) is the pressure of AgBr monomer, and  $p_{\text{trimer}}$  (Pa) is the pressure of AgBr trimer  
ii) Relative standard uncertainties (0.68 level of confidence) for temperature were less than 0.0012%.  
iii) Relative standard uncertainties (0.68 level of confidence) for vapor pressure were less than 11.1%.

**Table 3** Comparison of vapor pressure equations and thermochemical values for AgBr vapor over liquid AgBr

	$T$ (K)	$\ln(p/\text{Pa}) = -A/(T/\text{K}) + B$	
		A (K)	B (-)
Monomer	829.9–929.9	$23509 \pm 519$	$25.22 \pm 0.59$
Trimer		$19449 \pm 509$	$20.42 \pm 0.58$
Total		$21653 \pm 529$	$23.72 \pm 0.60$
Bloom et al. [2]	1240–1497	23871	24.96
Hildenbrand and Lau [3]	805–936	$20776 \pm 101$	$22.56 \pm 0.12$
Kelly [5]	1273–1473	$\ln(p \text{ (Pa)}) = -18720/(T \text{ (K)}) - 6.84 \log(T \text{ (K)}) + 43.13$	

i)  $T$  (K) is temperature,  $p$  (Pa) is pressure,  $A$  (K) and  $B$  (-) are constants in the vapor pressure fitting equation.

ii) Ranges for values obtained in the study represent the standard uncertainties (0.68 confidence level).

iii) Uncertainties for the reported values by Hildenbrand and Lau are “statistical errors derived from the fitting” [3].

iv) Bloom et al. [2] and Kelly [5] reported their values under the assumption that the only vapor species was a monomer, and Hildenbrand and Lau [3] reported an equation for the total pressure of AgBr as monomer + trimer.