

# Vaporization kinetics of $\text{Sb}_2\text{S}_3$ in argon fluid<sup>①</sup>

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**Abstract:** The vaporization kinetics of antimony trisulfide in argon fluid was studied with thermogravimetry at 873 - 1 173 K. A theoretical model was developed to calculate the overall rate constant and the mass transfer coefficient in gas phase. The experimental results show that the vaporization rate is enhanced with increasing temperature and argon flow-rate. The evaporation rate is mainly controlled by mass transport in the gas phase. The apparent activation energy for the process is found to be 55.54 kJ/mol. It is demonstrated that the mass transfer coefficient in gas phase is decreased with increasing temperature.

**Key words:**  $\text{Sb}_2\text{S}_3$ ; vaporization; kinetics

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## 1 INTRODUCTION

Antimony trisulfide is one of the most practically significant materials among the antimony sulfides in the industry. At present, in the production of antimony from sulfide ores, antimony trisulfide is volatilized into gas phase and then oxidized by oxygen in the gas phase. The antimony oxide produced is reduced to antimony in a reverberatory furnace<sup>[1]</sup>. Therefore it is important to investigate the evaporation process of antimony trisulfide under a special kind of atmosphere, and it has a quite significance for the industrial operation.

The evaporation mechanism of antimony trisulfide was investigated with different experimental methods by several authors<sup>[2-6]</sup>. It was demonstrated that the evaporation process is very complicated because the volatilization product may be composed of many species such as  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_4\text{S}_5$ ,  $\text{Sb}_4\text{S}_4$ ,  $\text{Sb}_4\text{S}_3$ ,  $\text{Sb}_2\text{S}_4$ ,  $\text{Sb}_3\text{S}_4$ ,  $\text{Sb}_2\text{S}_2$  and  $\text{SbS}_4$ . Obviously it is not possible to determine all kinetics parameters of these species. In this paper, the overall evaporation rate of pure antimony trisulfide is measured by thermogravimetry in argon and the reaction mechanism is discussed according to experimental results.

## 2 EXPERIMENTAL

Experimental apparatus is shown in Fig. 1. The purity of  $\text{Sb}_2\text{S}_3$  used in this investigation is greater than 99%. The carrier gas used is high-purity argon (> 99.999% Ar). In each run, 4 g of pure  $\text{Sb}_2\text{S}_3$  was placed in a corundum crucible with inner diameter of 2.6 cm and inner height of 3.8 cm. The crucible was suspended from

an electronic balance with a nichrome wire in the even temperature zone of furnace tube ( $d$  6 cm  $\times$  75 cm). The even temperature zone is 5 cm long. In experiments the apparatus was sealed, flushed with argon for 30 min and then heated under argon atmosphere. Temperature was measured by a Pt-Rd thermocouple (error  $\pm 1$  °C) and flow-rate of argon was controlled by a rotor flow-meter. After having reached the desired temperatures, the crucible was quickly put into the even temperature zone from the top of furnace tube and argon was introduced into the furnace tube from the bottom. The mass change of samples as a function of reaction time was recorded with a recorder.

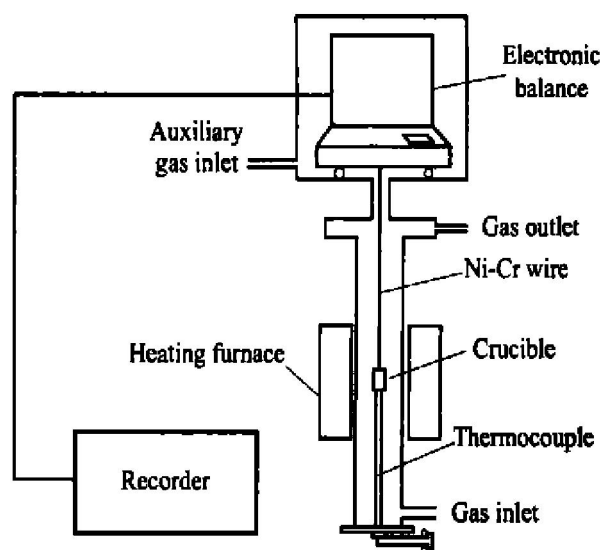


Fig. 1 Experimental setup

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### 3 THEORY OF EVAPORATION KINETICS

The vaporization process of antimony trisulfide has two steps: evaporation of antimony trisulfide at melt/gas interface, and transport of vapor through the gas boundary layer to the bulk gas phase.

According to Langmuir-Knudsen equation<sup>[7]</sup>, an expression for the evaporation of the antimony trisulfide at melt/gas interface is given by

$$N_{ev} = \frac{\alpha [p^+ (Sb_2S_3) - p^* (Sb_2S_3)]}{\sqrt{2\pi RTM(Sb_2S_3)}} \quad (1)$$

where  $\alpha$  is condensation coefficient which can generally be taken as 1.0 for pure melt,  $R$  is gas constant,  $T$  is temperature,  $M(Sb_2S_3)$  is relative molecular mass of  $Sb_2S_3$ ,  $p^* (Sb_2S_3)$  is the actual partial pressure of gaseous  $Sb_2S_3$  on the interface of a gas phase boundary layer,  $p^+ (Sb_2S_3)$  is the equilibrium partial pressure above the melt surface and can be expressed as<sup>[8]</sup>

$$\ln p^+ (Sb_2S_3) = 20.066 - \frac{11604}{T} \quad (773 K \leq T \leq 173 K) \quad (2)$$

Defining the  $K_E$  as

$$K_E = \frac{1}{\sqrt{2\pi RTM(Sb_2S_3)}} \quad (3)$$

Eqn. (1) becomes

$$N_{ev} = K_E [p^+ (Sb_2S_3) - p^* (Sb_2S_3)] \quad (4)$$

The rate of mass transport in the gas phase away from the melt surface through the gas boundary layer can be represented by

$$N_{gas} = \frac{k_G}{RT} [p^* (Sb_2S_3) - p^b (Sb_2S_3)] \quad (5)$$

where  $k_G$  is the gas phase mass transfer coefficient,  $p^b (Sb_2S_3)$  is the partial pressure of gaseous  $Sb_2S_3$  in bulk gas which can be neglected in this investigation because the evaporation rate of  $Sb_2S_3$  is much slower than the flow rate of argon. Hence Eqn. (5) can be simplified as

$$N_{gas} = K_U p^* (Sb_2S_3) \quad (6)$$

$$K_U = k_G / RT \quad (7)$$

According to a quasi-steady-state assumption, one has

$$N_o = N_{ev} = N_{gas} \quad (8)$$

Combining Eqn. (4) with Eqn. (6) gives the overall evaporation rate equation:

$$N_o = \frac{p^+ (Sb_2S_3)}{\sqrt{2\pi RTM(Sb_2S_3)} + \frac{RT}{k_G}} = \frac{p^+ (Sb_2S_3)}{\frac{1}{K_E} + \frac{1}{K_U}} \quad (9)$$

let

$$\frac{1}{K} = \frac{1}{K_E} + \frac{1}{K_U} \quad (10)$$

Eqn. (9) becomes

$$N_o = K p^+ (Sb_2S_3) \quad (11)$$

Eqn. (11) indicates that the volatilization rate of

$Sb_2S_3$  is a constant if temperature and carrier gas flow rate keep constant.

### 4 RESULTS AND DISCUSSION

#### 4.1 Effect of carrier gas flow rate

The effect of carrier gas flow-rate on the vaporization of  $Sb_2S_3$  at 1 023 K is shown in Fig. 2. It is evident that the mass loss of  $Sb_2S_3$  is a linear function of time, i. e. the volatilization rate of  $Sb_2S_3$  is a constant at constant temperature and carrier gas flow-rate. This result is in good agreement with Eqn. (11). Fig. 2 also indicates that the vaporization rate of  $Sb_2S_3$  is enhanced with increasing argon flow rate, which implies that the mass transport in gas phase plays an important role in the evaporation process.

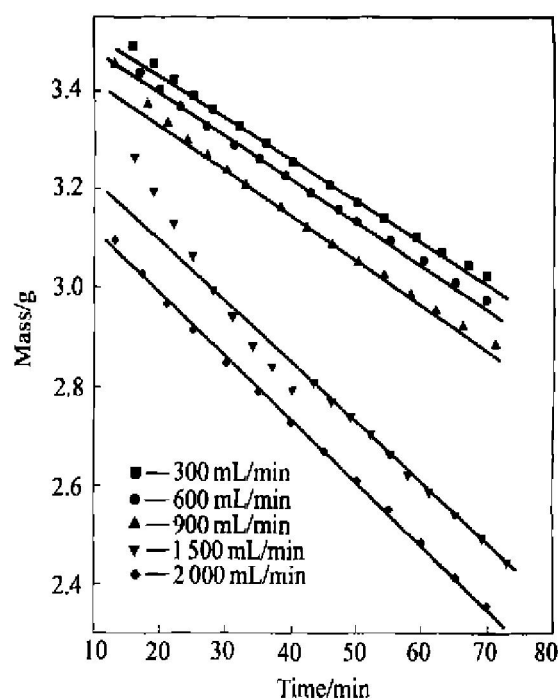


Fig. 2 Effect of argon flow-rate on evaporation of  $Sb_2S_3$  at 1 023 K

From Fig. 2 the overall evaporation rate  $N_o$  can be calculated. Substitution of  $N_o$  into Eqn. (11) gives apparent rate constant  $K$ . According to Eqns. (3) and (10),  $K_E$  and  $K_U$  can be also obtained. The results calculated are summarized in Table 1.

From Table 1 it can be seen that  $K_U$  is much smaller than  $K_E$ , i. e. the evaporation process is mainly controlled by mass transport in the gas phase. In this case, the evaporation rate may be simplified as

$$N_o \approx K_U p^+ (Sb_2S_3) = \frac{k_G}{RT} p^+ (Sb_2S_3) \quad (12)$$

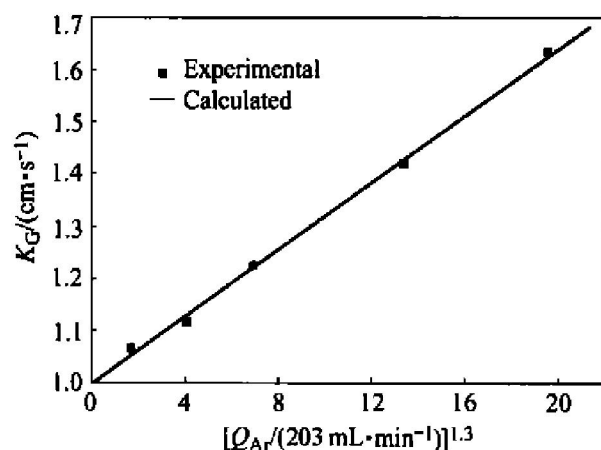
From Eqn. (7) the mass transfer coefficient in gas phase  $k_G$  can be calculated for the various flow rates of

**Table 1** Effect of argon flow-rate on evaporation parameters at 1 023 K

$Q_{\text{Ar}}/$ ( $\text{mL} \cdot \text{min}^{-1}$ )	$N_o/(10^{-7} \text{mol} \cdot$ $\text{cm}^{-2} \cdot \text{s}^{-1})$	$K/(10^{-11} \text{mol} \cdot$ $\text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1})$	$K_E/(10^{-7} \text{mol} \cdot$ $\text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1})$	$K_U/(10^{-10} \text{mol} \cdot$ $\text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1})$	$k_G/$ ( $\text{cm} \cdot \text{s}^{-1}$ )	$\delta/$ cm
300	0.766	1.250	7.418	1.250	1.063	0.672
600	0.802	1.308	7.418	1.308	1.113	0.642
900	0.881	1.437	7.418	1.437	1.222	0.584
1500	1.023	1.668	7.418	1.668	1.419	0.503
2000	1.178	1.921	7.418	1.921	1.634	0.437

carrier gas. By regression analysis, as shown in Fig. 3, the relationship between  $k_G$  and argon flow-rate  $Q$  at 1 023 K can be expressed as

$$k_G = 3.2235 \times 10^{-5} Q^{1.3} + 0.9956 \quad (300 \text{ mL/min} \leq Q \leq 2000 \text{ mL/min}) \quad (13)$$

**Fig. 3** Effect of argon flow-rate on  $k_G$ 

This result is reasonable because the mass transfer coefficient has a close relation with the flow rate of carrier gas according to the following equation<sup>[9,10]</sup>:

$$Sh = \alpha Re^a Sc^\beta + b \quad (14)$$

where  $Sh (= k_G d / D)$  is Sherwood number,  $Re (= \rho l u / \mu)$  is Reynolds number,  $Sc (= \mu / \rho D)$  is Schmidt number,  $u$  is average velocity of argon,  $\rho$  is density of argon,  $d$  is diameter of furnace tube,  $D$  is inter-diffusivity,  $\mu$  is viscosity of argon;  $a$ ,  $b$ ,  $\alpha$  and  $\beta$  are empirical constants. When temperature is kept constant,  $D$ ,  $\rho$  and  $\mu$  will be changeless. So from Eqn. (14), one has

$$k_G \propto Q^\alpha \quad (15)$$

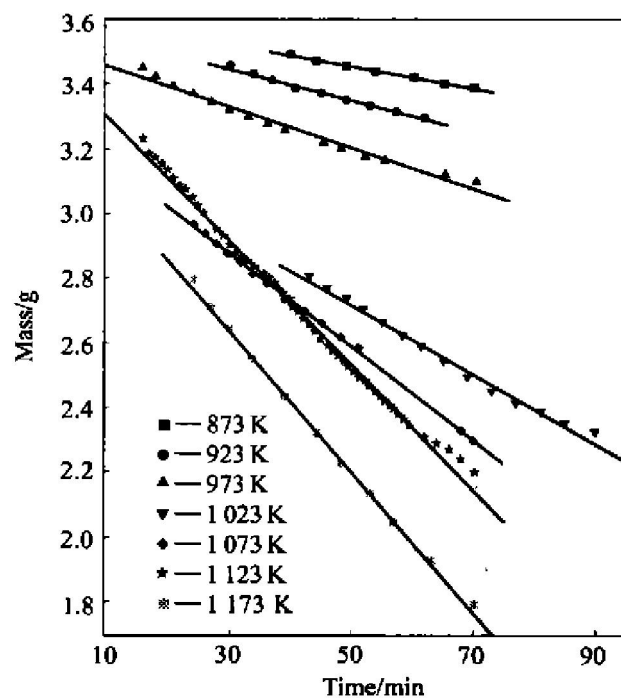
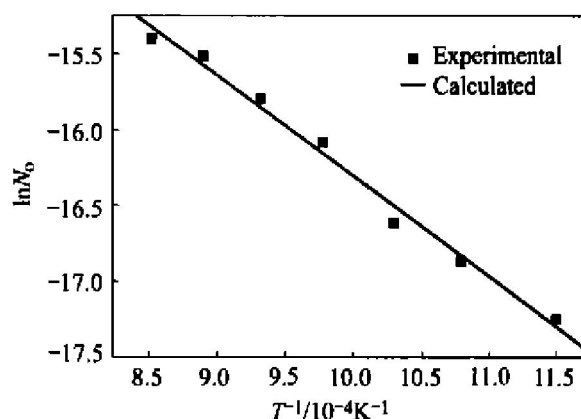
$\alpha = 1.3$  for the present study.

## 4.2 Effect of temperature

The effect of temperature on the vaporization rate of  $\text{Sb}_2\text{S}_3$  is shown in Fig. 4, from which the overall volatilization rate  $N_o$  of  $\text{Sb}_2\text{S}_3$  at different temperatures can be calculated. Plotting  $\ln N_o$  against  $1/T$ , as shown in Fig. 5, gives the temperature dependence of  $N_o$  as the following:

$$\ln N_o = -\frac{6680}{T} - 9.63 \quad (16)$$

From Eqn. (16) the apparent activation energy for the process is found to be  $E = 55.54 \text{ kJ/mol}$ .

**Fig. 4** Effect of temperature on volatilization of  $\text{Sb}_2\text{S}_3$ **Fig. 5**  $\ln N_o$  vs  $1/T$ 

According to Eqn. (2), the enthalpy of vaporization for  $\text{Sb}_2\text{S}_3$  can be estimated at  $\Delta H_v = 96.48 \text{ kJ/mol}$ . The apparent activation energy for the vaporization process should be approximately equal to the enthalpy of vaporization if the rate-determining step is the surface evaporation process<sup>[11]</sup>. It is obvious that  $E$  is appreciably smaller than  $\Delta H_v$  in the

present study, suggesting that the evaporation rate of  $\text{Sb}_2\text{S}_3$  is mainly controlled by the mass transport in the gas phase rather than by the evaporation at the gas/liquid interface. Thus,  $N_o$  is determined by  $p^+$  ( $\text{Sb}_2\text{S}_3$ ) and  $k_G$ . Higher temperature gives a higher vapor pressure of  $\text{Sb}_2\text{S}_3$  and hence results in a higher evaporation rate. The effect of temperature on the mass transfer coefficient  $k_G$  in gas phase can be discussed as follows.

The mass transfer coefficient in gas phase is given by

$$k_G = \frac{D_{AB}}{\delta} \quad (17)$$

where  $\delta$  is the thickness of gas boundary layer that is related to the viscosity and flow rate of carrier gas.

$D_{AB}$  is diffusion coefficient of  $\text{Sb}_2\text{S}_3$  in argon, which can be calculated by Chapman-Enskog equation<sup>[12]</sup>:

$$D_{AB} = \frac{1.858 \times 10^{-8} T^{3/2} (1/M_A + 1/M_B)^{1/2}}{p \sigma_{AB}^2 \Omega_D} \quad (18)$$

where the subscripts A and B are molecular species A and B,  $M$  is relative molecular mass,  $p$  is pressure,  $\Omega_D$  is collision integral for diffusion which can be expressed as a dimensionless function of temperature and the intermolecular potential between molecule species A and B,  $\sigma_{AB}$  is collision diameter,  $T$  is temperature.

The viscosity of carrier gas can be calculated by<sup>[12]</sup>

$$\mu = \frac{2.6693 \times 10^{-5} (MT)^{1/2}}{\sigma^2 \Omega^*} \quad (19)$$

where  $\Omega^*$  is collision integral for viscosity. The corresponding kinematic viscosity  $\nu$  can be expressed as

$$\nu = \mu / \rho \quad (20)$$

All the evaporation parameters concerned can be obtained from experimental results or calculated by the above equations, as shown in Table 2. It demonstrates that the mass transfer coefficient  $k_G$  in gas phase decreases with increasing temperature. The same phenomenon was also observed by Ozberk and Outhier<sup>[7]</sup> in the vaporization process of impurities from liquid copper. This phenomenon is due to the fact that the effective thickness of gas boundary layer increases with the kinematic viscosity of carrier gas.

Through regression analysis, as shown in Fig. 6, the relationship between  $\delta$  and  $\nu$  can be described with the

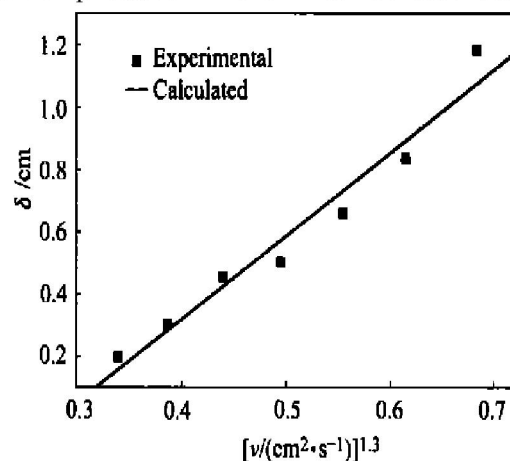


Fig. 6 Effect of kinematic viscosity on thickness of gas boundary layer

following empirical equation:  $\delta = 2.6956\nu^{1/3} - 0.7619$  (21)

This result can be explained by Eqn. (14). According to calculation, the Schmidt number in Eqn. (14) is almost changeless when temperature changes. If gas flow rate keeps constant, Eqn. (14) becomes

$$\delta \propto \nu^\alpha \quad (\alpha = 1.3) \quad (22)$$

Since  $\nu$  increases with temperature, an increase in temperature will make  $\delta$  increase and hence cause  $k_G$  decrease. Substitution of Eqns. (2) and (15) into Eqn. (12) gets

$$\ln k_G = \frac{4.923}{T} + \ln T - 13.762 \quad (23)$$

## 5 SUMMARY

The evaporation rate of  $\text{Sb}_2\text{S}_3$  under argon atmosphere is controlled by the mass transport through the gas boundary layer. The evaporation rate is appreciably enhanced with increasing the flow rate of carrier gas and the temperature. Increasing the flow rate gives rise to an increase in the thickness of the gas boundary layer.

Table 2 Effect of temperature on evaporation parameters ( $Q_{Ar} = 1500 \text{ mL/min}$ )

$T/K$	$N_o / (10^{-7} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1})$	$p^+ (\text{Sb}_2\text{S}_3) / \text{Pa}$	$K / (10^{-11} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1})$	$K_E / (10^{-7} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1})$	$K_U / (10^{-11} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1})$	$k_G / (\text{cm} \cdot \text{s}^{-1})$	$D / (\text{cm}^2 \cdot \text{s}^{-1})$	$\delta / \text{cm}$	$\nu / (\text{cm}^2 \cdot \text{s}^{-1})$
873	0.322	881	3.767	8.030	3.767	2.734	0.534	0.195	0.435
923	0.468	1795	2.608	7.812	2.608	2.001	0.591	0.295	0.482
973	0.607	3426	1.772	7.610	1.772	1.433	0.651	0.454	0.531
1023	1.023	6132	1.668	7.418	1.668	1.419	0.714	0.503	0.582
1073	1.367	10359	1.320	7.246	1.320	1.177	0.778	0.661	0.635
1123	1.816	16835	1.079	7.082	1.079	1.007	0.844	0.838	0.688
1173	2.052	25998	0.789	6.930	0.789	0.770	0.914	1.187	0.745

rease in mass transfer coefficient in gas phase, while raising temperature mainly leads to an increase in the vapor pressure of  $\text{Sb}_2\text{S}_3$ . The apparent activation energy for the evaporation process is estimated as 55.54 kJ/mol. It is found that the effective thickness of gas boundary layer is increased with temperature. As a result, the mass transfer coefficient in gas phase will decrease with increasing temperature.

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