

KINETICS OF STIBNITE (Sb_2S_3) OXIDATION AT ROASTING TEMPERATURES

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Abstract

Experimental work on the oxidation of stibnite (Sb_2S_3) was carried out at temperatures between 350 and 500 °C and oxygen partial pressures between 1.01 and 21.28 kPa by using a thermogravimetric analysis method. The oxidation rate of stibnite was significantly influenced by both temperature and partial pressure of oxygen. Stibnite oxidized in one step to valentinite (Sb_2O_3) and neither stibnite nor valentinite showed a detectable rate of volatilization at these low temperatures. The oxidation reaction of stibnite was analyzed by using the shrinking core model and it was found that the rate of reaction was controlled by the surface chemical reaction and it was of 3/5 order with respect to the oxygen partial pressure. The intrinsic rate constants were determined and an activation energy value of 90.3 kJ/mol was obtained for the range of temperature studied.

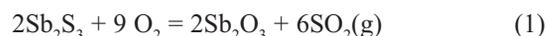
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1. Introduction

The behavior of minor elements such as As, Sb and Bi in copper smelting and also in other nonferrous smelting has been the subject of industrial concern in the past decades, not only because the handling of these impurities has a risk of atmospheric contamination but also because they can have a detrimental effect on the quality of the final metal [1, 2]. Consequently, if the concentration of these minor elements in the concentrates is higher than the permissible limits for the treatment by conventional smelting methods, the concentrates must be pretreated prior to processing in the smelter. The common methods used for the pretreatment of dirty concentrates include roasting processes and leaching processes. Roasting has been an effective method for preferential removal of the minor components from the concentrates, particularly arsenic and antimony, in the form of volatile compounds at high temperatures [3]. Besides temperature, another parameter that has an important effect on the removal of impurities in roasting is the type of atmosphere, which should maximize the vapor pressure of the impurity compounds that are to be removed. Thus the common type of atmospheres used in roasting includes oxidizing, inert and reducing.

Antimony's main stable mineral is stibnite (Sb_2S_3) and few studies have been reported on the rate of oxidation-volatilization of this mineral at roasting or higher temperatures. On this matter, Komorova et al.

[4] studied the vaporization of several antimony containing compounds, among them synthetic Sb_2S_3 , in nitrogen atmosphere using the transportation method. They found that in the temperature range of 600 °C to 824 °C, Sb_2S_3 vaporized as antimony trisulfide. Zivkovic et al. [5] studied the non-isothermal oxidation of Sb_2S_3 with air in the temperature range of 200 °C to 800 °C. From simultaneous DTA-TG-DTG analysis, they concluded that the oxidation occurred by the following sequence of reactions:



These authors reported activation energy values calculated by the Ozawa method of 90 and 97 kJ/mol for reactions (1) and (2), respectively.

Recently, Padilla et al. [6] carried out an isothermal study of the volatilization of stibnite in nitrogen-oxygen atmospheres in the temperature range of 700 to 1150 °C and they were able to determine the reaction mechanism in this temperature range. Their results indicated that in the presence of oxygen, antimony could be volatilized efficiently as Sb_2O_3 in the temperature range of 900 °C to 950 °C in a gas phase with 1 to 5% oxygen. At higher oxygen concentrations the antimony volatilization was hindered by the formation of non-volatile SbO_2 . Furthermore, in highly oxidizing atmospheres

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effective volatilization of antimony could only be achieved at temperatures higher than 1150 °C where SbO_2 becomes unstable and decomposes into $\text{SbO}(\text{g})$ and $\text{O}_2(\text{g})$. At these high temperatures (700 °C to 1150 °C), Sb_2S_3 and Sb_2O_3 are in the liquid state since the melting points of stibnite and antimony trioxide are 550 °C and 656 °C, respectively [7]. Since roasting processes are carried out normally at temperatures where the minerals must maintain their solid structure without melting or sintering for efficient transformations of the compounds, there is a need of experimental data on the oxidation behavior of Sb_2S_3 at temperatures lower than the melting point of this mineral.

Considering the above, the present investigation was concerned with the oxidation of solid stibnite (Sb_2S_3) in mixtures of nitrogen-oxygen of various compositions and the main objective was the determination of the kinetics of oxidation of stibnite at temperatures below the melting point of Sb_2S_3 .

2. Experimental Work

The present investigation was carried out by using a high grade stibnite concentrate. This concentrate was prepared from large natural stibnite crystals, which were crushed, ground and classified by sieving into three size fractions -106+75 μm , -75+53 μm , and -53+38 μm with average sizes of 90, 63 and 45 μm , respectively. Most of the experiments were conducted using the fraction with average size of 90 μm , which according to the chemical analysis contained 67.5% Sb, 0.03% Pb, and siliceous gangue minerals. Based on this analysis the Sb_2S_3 content was calculated as 94.8%. The X-ray diffraction (XRD) analysis of the antimony sulfide samples were performed using a Rigaku (model Geiger Flex) copper anode spectrometer. The results confirmed that the stibnite concentrate was nearly pure antimony trisulfide (Sb_2S_3).

The oxidation experiments of the Sb_2S_3 samples were conducted in a custom-built thermogravimetric analysis apparatus that essentially consisted of a high temperature vertical furnace which contained a quartz reaction tube (45 mm inner diameter), a Sartorius microbalance model ME235P with sensitivity 0.00001 g mounted on top of the reaction tube, and a personal computer for data storage. The setup comprised also a gas delivery system for provision of various nitrogen-oxygen mixtures. The temperature of the sample was measured by means of a chromel/alumel thermocouple placed in the constant temperature region of the reaction tube, which was a zone about 90 mm in length located in the center of the tube. Previous to the oxidation experiments, the thermogravimetric system was tested for adequacy by heating activated carbon of known chemical

composition in pure nitrogen and in oxidizing atmospheres.

In a typical experiment, the reaction temperature was firstly set and stabilized; then, 50 mg of a stibnite sample contained in a 1.3 ml crucible (11mm ID x 14 mm H) was rapidly introduced in the constant temperature region of the reaction tube. Immediately after introducing the crucible into the reaction tube, the instantaneous weight and temperature of the sample were recorded continuously until the weight of the sample remained constant. The total pressure of the reaction system was that of atmospheric pressure (101.3 kPa) and the degree of oxidation of the stibnite was determined from the initial and instantaneous weight of the sample. The reacted solids were analyzed by XRD to determine the reaction solid products. In some cases, partially reacted samples were obtained at specific reaction times for the determination of possible intermediate compounds formed during the oxidation of stibnite. The sampling procedure consisted of lifting the crucible rapidly to the upper part of the reaction tube where the sample was quenched with a flow of nitrogen; the quenching time for the most part was about 20 s. Afterwards, the sample was removed rapidly from the reaction tube for final cooling in a desiccator.

3. Results

Preliminary experiments were carried out at various temperatures to define the appropriate range of experimental conditions for the determination of the intrinsic kinetics of the oxidation of stibnite at roasting temperatures. For this purpose, several experiments were carried out using 50 mg of a loose-bed of stibnite samples with average particle size of 90 μm . These samples were reacted at constant temperature with an oxidizing atmosphere (partial pressure of oxygen of 21.28 kPa) under various gas velocities to determine the conditions in which the external mass transfer did not affect the stibnite oxidation rate. The result obtained for flow rates in the range of 0.6 to 1.5 L/min is shown in Figure 1, where the data were plotted as the fractional weight loss of the sample, defined as $\Delta W / W_0$, where ΔW is the weight loss of the sample equal to $(W_0 - W_t)$, and W_0 and W_t are the initial weight of the sample and the weight at time t , respectively. Thus we can observe in Figure 1 that the gas velocity did not affect the oxidation rate of the stibnite. This data indicates clearly that in the range of flow rates used, there are not mass transfer constraints in the oxidation reaction when using a shallow bed of stibnite sample. Therefore, 50 mg samples and 1L/min gas flow rate were considered appropriate for the subsequent kinetic experiments.

In Figure 1, it can also be observed that the

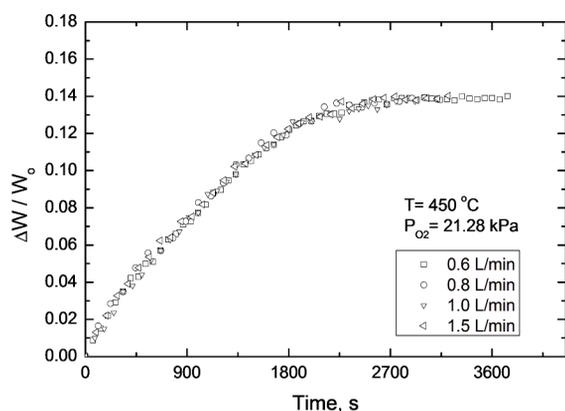


Figure 1. Fraction of weight loss vs. time in the stibnite oxidation illustrating the negligible effect of mass transfer.

experimental data on the oxidation of stibnite levels off when the sample weight loss fraction reached a value of 0.14. Additional experiments carried out at various temperatures and oxygen partial pressures showed the same behavior of gradual weight loss up to a value 0.14 where the curves leveled off. The theoretical weight loss fraction for complete oxidation of Sb_2S_3 to Sb_2O_3 according to the reaction (1) is 0.141. This suggests that in the range of temperature studied the oxidation of Sb_2S_3 occurs directly to Sb_2O_3 till completion according to reaction (1). To verify this presumption a partially reacted sample was obtained from an experiment conducted at 450 °C, 21.28 kPa O_2 , and 1080 s of reaction for XRD analysis. The resulting spectrum is shown in Figure 2, where it can be observed diffraction lines for the remaining unreacted stibnite and strong diffraction lines for the product valentinite (Sb_2O_3), as expected. Valentinite is dimorphous with senarmontite which has also been identified at temperatures higher than 550 °C. Therefore, these results confirm that the oxidation of

stibnite with oxygen at temperatures below the melting point of stibnite proceeds according to reaction (1) with the formation of well crystallized Sb_2O_3 , which did not volatilize noticeably at these low temperatures. Consequently, the advance of reaction (1) can be accurately determined from the experimental weight loss data.

Further oxidation of Sb_2O_3 to SbO_2 , which would have resulted in a weight gain of the sample, was not observed in the range of temperatures studied here, even for the experiments with partial pressure of oxygen of 21.28 kPa and extended reaction times.

3.1 Effect of reaction temperature

The effect of temperature on the oxidation of stibnite was studied in the range of 300 °C to 500 °C, under partial pressures of oxygen in the range of 1.01 to 21.28 kPa. Since in this range of temperature, both the reactant Sb_2S_3 and the product Sb_2O_3 are solid, the oxidation reaction occurred without forming liquid phases. The results for the partial pressure of 21.28 kPa are shown in Figure 3, where the fraction of stibnite conversion is shown as a function of time. The conversion was calculated as $\alpha = \Delta W / \Delta W_{\text{th}}$, where ΔW is the experimental weight loss and ΔW_{th} is the theoretical weight loss for complete conversion according to reaction (1). In this figure, it can be seen that temperature has a strong influence on the rate of oxidation of stibnite. It was determined that the oxidation of stibnite was negligible at 300 °C and the oxidation was very slow at 350 °C while at 500 °C the oxidation was very rapid. Similar results were obtained when the stibnite was reacted under the other partial pressures of oxygen. The strong dependency of the oxidation rate on temperature suggests that the oxidation of stibnite is controlled by a surface chemical reaction.

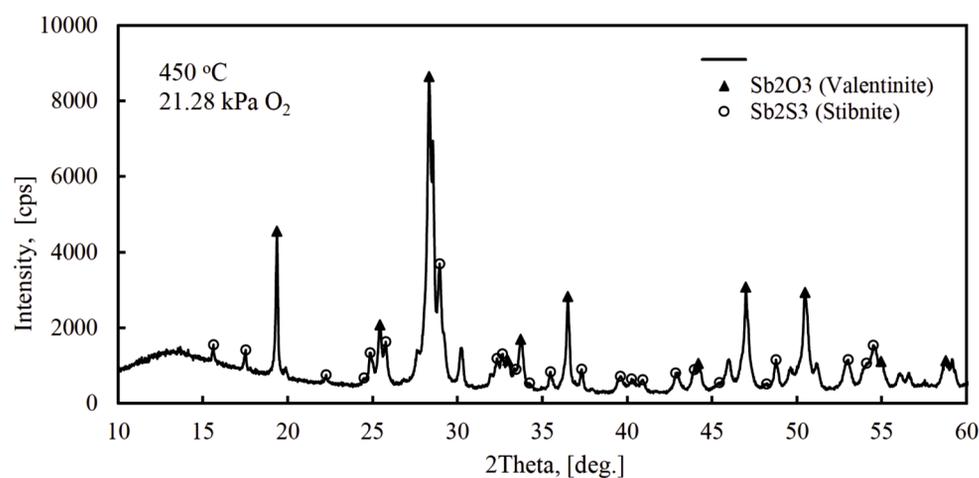


Figure 2. XRD spectrum (Cu K α) of a partially oxidized stibnite sample under the conditions shown in the figure.

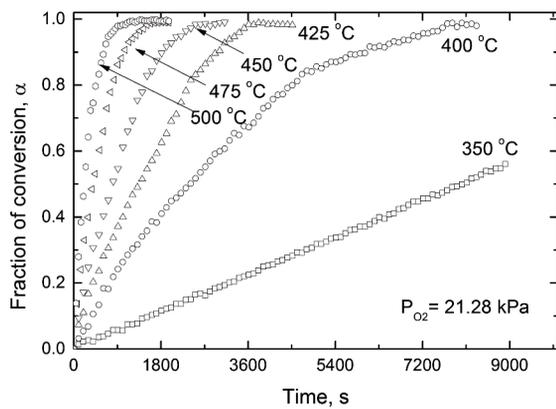


Figure 3. Oxidation of stibnite with average particle size 90 μm as a function of temperature in 21.28 kPa of partial pressure of oxygen.

3.2. Effect of the oxidizing atmosphere

The influence of oxygen partial pressure on the rate of oxidation of stibnite was studied in the range of 1.01 to 21.28 kPa O_2 . The experiments were conducted at 450, 475 and 500 $^\circ\text{C}$ using the stibnite size fraction with average particle size of 90 μm . The data of conversion versus time obtained at 450 $^\circ\text{C}$ are presented in Figure 4, where it can be clearly seen that there is a strong dependency of the Sb_2S_3 oxidation rate on the oxygen content of the gas phase. Similar results were obtained for the temperatures of 475 and 500 $^\circ\text{C}$ (data not shown). From the data shown in Figures 3 and 4, it can be concluded that antimony compounds do not volatilize at the temperatures and pressures studied.

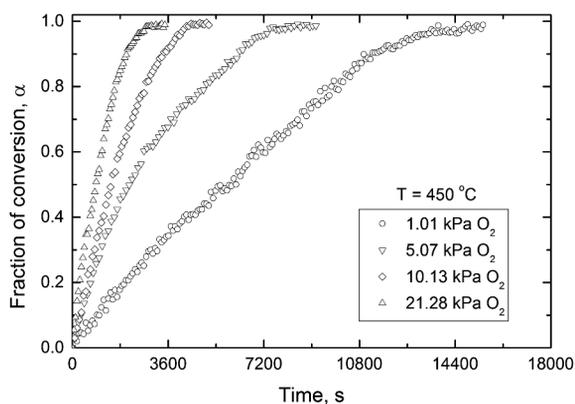


Figure 4. Oxidation of stibnite with average particle size of 90 μm as a function of partial pressure of oxygen at 450 $^\circ\text{C}$.

3.3. Effect of particle size of stibnite

To determine the effect of the stibnite particle size on the rate of oxidation, experiments were carried using the three different average particle sizes: 90

mm, 63 mm and 45 mm. The results are shown in Figure 5. As expected, there is an appreciable effect of the particle size on the oxidation rate; therefore, this result supports the proposition that the oxidation of stibnite is controlled by chemical reaction as opposed to diffusion processes.

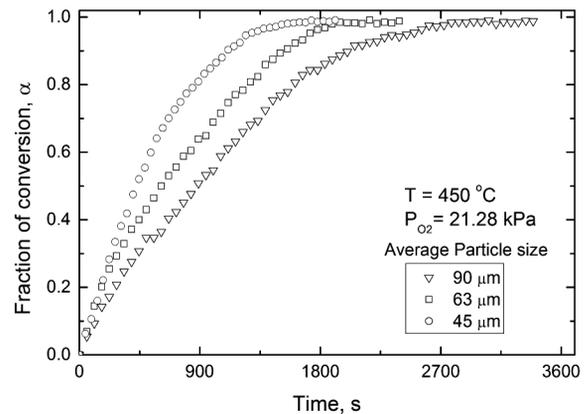


Figure 5. Oxidation of stibnite as a function of time and initial particle size. Experimental conditions were 450 $^\circ\text{C}$ and 21.28 kPa O_2 .

3.4. Oxidation Kinetics

The experimental data obtained on the oxidation of stibnite was analyzed using the well-known shrinking core model for surface reaction control [8]. For particles with a narrow range of sizes (as obtained by sieving) and constant partial pressure of oxygen, the integrated model equation can be written as:

$$1 - (1 - \alpha)^{1/3} = k_{\text{app}} t \quad (3)$$

where α is the conversion, k_{app} is the apparent reaction rate constant and t is the reaction time. Thus, the apparent rate constant depends on the temperature, partial pressure of the gaseous reactant and the particle size of the solid reactant. The dependency can be described by the following expression [8, 9]:

$$k_{\text{app}} = \frac{b \cdot k \cdot P_{\text{O}_2}^m}{r_0} \quad (4)$$

where, b is a stoichiometric constant, k is the intrinsic kinetic constant, m is the reaction order with respect to the partial pressure of oxygen, and r_0 is the radius of the solid reactant particle.

Figure 6 shows a plot of $1 - (1 - \alpha)^{1/3}$ as a function of time for the conversion data shown previously in Figure 3. As can be seen in the figure, there is a good linear fitting of the data demonstrating the adequacy of the kinetic equation (3). Thus the apparent reaction rate constants can be calculated from the slopes of the lines in Figure 6.

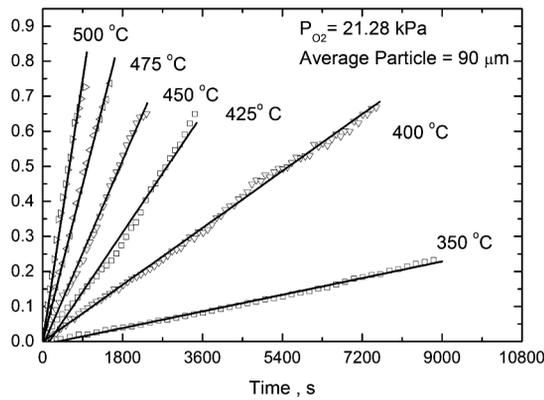


Figure 6. Oxidation rate of stibnite in the temperature range of 350 °C - 500 °C, under 21.28 kPa O_2 .

Identical approach was used for the data regarding the concentration of the oxygen in the gas phase shown earlier in Figure 4. The result of plotting these data in accordance with equation (3) is shown in Figure 7. The apparent rate constants obtained from the slopes of the lines obtained from Figure 7 and similar plots for temperatures of 475 and 500 °C were used to determine the dependency of the apparent rate constant on the partial pressure of oxygen. Such a plot is shown in Figure 8, where it can be observed a linear relationship between $\ln(k_{app})$ vs. $\ln(P_{O_2})$ at all the temperatures with a slope equal to 3/5. This result indicates that the apparent reaction rate constant is of 3/5 order with respect to the concentration of oxygen in the gas phase. Furthermore, the values of the apparent kinetic constant for various particle sizes obtained from Figure 9 were used to verify the dependence of the kinetic constant on the initial radius of the particles. As seen in Figure 10, the apparent kinetics constant is proportional to $1/r_o^2$, which further support the adequacy of the kinetic model used. Consequently, the intrinsic kinetic constant k for the various temperatures can now be calculated using the values of the apparent kinetic constants obtained from

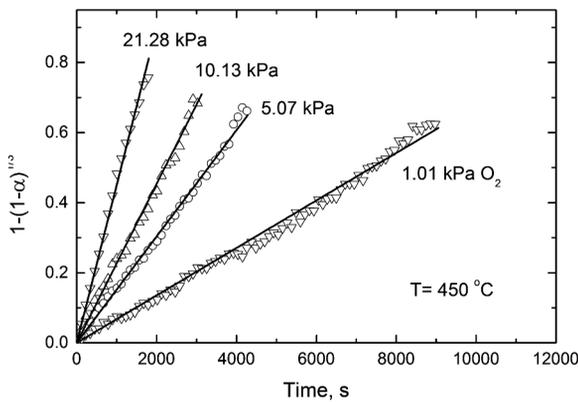


Figure 7. Stibnite oxidation rate as a function of partial pressure of oxygen.

Figure 6, the value of m equal to 0.6, and the stoichiometric constant b equal to 2/9, according to the stoichiometry of reaction (1). Table 1 shows both the apparent and the intrinsic rate constants for the temperatures studied.

Thus, an Arrhenius plot was drawn by using the intrinsic kinetic constants given in Table 1. The result

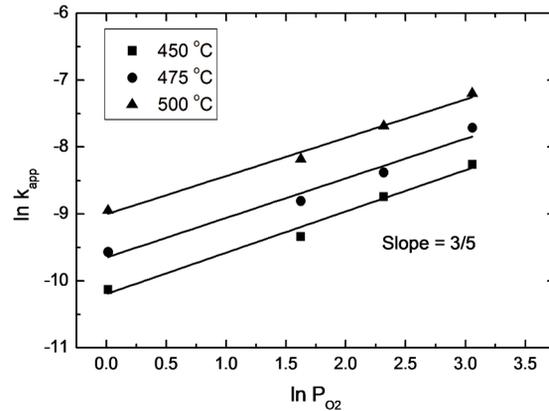


Figure 8. Dependence of the apparent rate constants on the partial pressure of oxygen.

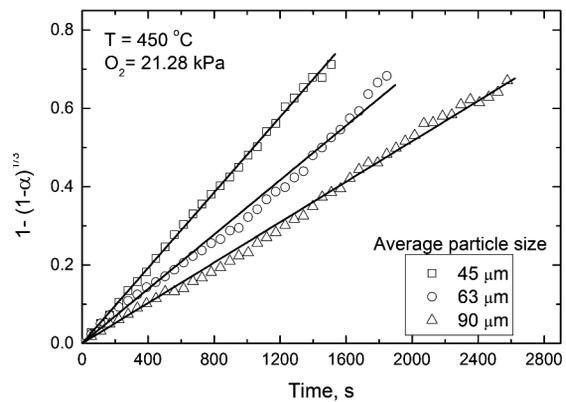


Figure 9. Stibnite oxidation rate as a function of the initial particle size.

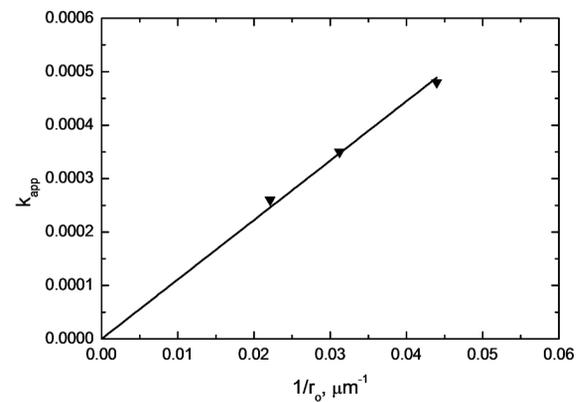


Figure 10. Dependence of the apparent rate constants on the inverse of initial particle size.

Table 1. Rate constants for the oxidation of stibnite in the temperature range of 350 to 500 °C for 21.28 kPa of O₂.

T, [°C]	k _{app} , [s ⁻¹]	k, [s ⁻¹ (kPa) ^{-0.6} m]
350	5.00E-05	8.08E-10
400	9.00E-05	2.91E-09
425	1.60E-04	5.17E-09
450	2.60E-04	8.41E-09
475	4.50E-04	1.45E-08
500	7.60E-04	2.46E-08

is depicted in Figure 11, where it can be observed that a linear relationship exists between the rate constant and the inverse of temperature for the range studied of 350 to 500 °C. The linear regression of the data yielded an activation energy value of 90.3 kJ/mol for 21.28 kPa of O₂. The same value for the activation energy was determined for the other partial pressures of oxygen. The activation energy value found in this research is in excellent agreement with the value of 90 kJ/mol reported by Zivkovic et al.[5], who determined the activation energy in a non-isothermal study of the oxidation of synthetic stibnite in the range 200 to 450 °C carried out in a DTA-TG-DTG system. Thus the activation energy found in this research is in accordance to what is expected in a process controlled by a chemical reaction. In summary, the intrinsic kinetic constant for the oxidation of stibnite in the presence of oxygen in the range 350 to 500 °C can be expressed as:

$$k = 0.0299 \exp\left(-\frac{10867}{T}\right) \text{ s}^{-1} \text{ kPa}^{-0.6} \text{ m} \quad (5)$$

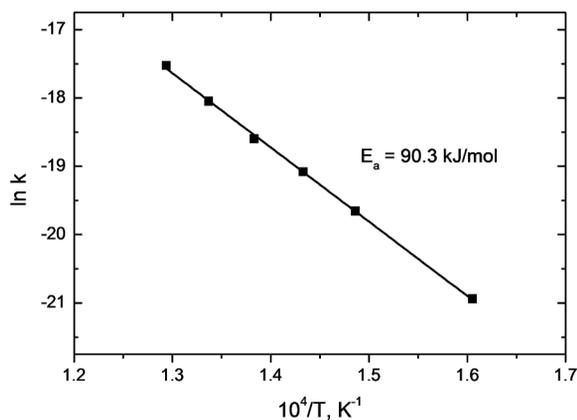


Figure 11. Dependence of the intrinsic kinetic constant k ($\text{s}^{-1} \cdot \text{kPa}^{-0.6} \cdot \text{m}$) on the temperature for the oxidation of stibnite to valentinite in 21.28 kPa O₂ atmosphere.

4. Conclusions

Based on the experimental evidence obtained in this work the following can be concluded:

The oxidation of stibnite in oxygen-nitrogen atmospheres in the range of temperatures of 300 °C to 500 °C occurs in a single step to produce Sb₂O₃(s) and SO₂(g) as reaction products. Temperature and partial pressure of oxygen affect significantly the oxidation rate and the antimony volatilization, either as Sb₂S₃ or Sb₂O₃, in this range of temperatures was negligible.

The kinetics of the oxidation of stibnite was analyzed by using the shrinking core model. It was found that the oxidation reaction is controlled by a surface chemical reaction and is of 3/5 order with respect to the oxygen partial pressure. The activation energy determined in the range of temperatures studied was 90.3 kJ/mol.

Acknowledgements

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