# Kinetics and mechanism of As$_2$S$_2$ oxidation

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*Abstract*: The kinetics of realgar (As$_2$S$_2$) oxidation was studied under isothermal and non-isothermal conditions. The obtained values of the activation energy indicate that the process occurs in the kinetic domain with the realgar particles being converted to As$_2$O$_3$ and As$_4$O$_6$ (g). The very fast reaction rates were limited by the chemical reaction. The kinetic equation was found to be: $-\ln (1-\alpha) = 4.56 \times 10^3 \times e^{(-8780/T)} \times t$. The proposed reaction mechanism and chemical transformation investigated by ICP–AES, EDXRF and thermal analysis are discussed.

*Keywords*: thermal analysis, activation energy, As$_2$S$_2$, EDXRF, ICP–AES.

## INTRODUCTION

Though known since ancient times,[1,2] the As–S system is a subject of interest for numerous researchers. The reason for this is the insufficient consideration of the mechanisms of the oxidation reactions occurring in this system, as well as a lack of complete databases with thermodynamic and kinetic parameters describing the oxidation processes of compounds from this system. It should also be mentioned that the literature data for temperatures significant for describing the oxidation mechanism differ depending on the source. For example, for compounds As$_2$O$_3$ and As$_2$O$_5$, which are the main products of oxidation of compounds from the As–S system, in the Kirk–Othmer Encyclopedia of Chemical Technology,[3] the temperature of As$_2$S$_2$ sublimation is 135 ºC and for As$_2$O$_5$ dissociation 300 ºC. According to the Handbook of Chemistry and Physics,[4] As$_2$O$_3$ sublimate at 193 ºC and As$_2$O$_5$ dissociate at 315 ºC.

A number of authors studied natural as well as synthetic realgar (As$_2$S$_2$), also present in the literature with the formula AsS or As$_4$S$_4$.

The degree of dissociation of arsenic sulfide (AsS) was determined by measuring the vapor pressure change with temperature.[6] The sulfide was synthesized by heating

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chemically pure elements at 500–600 ºC for 2 h. After homogenization under vacuum at 300–320 ºC, the compound contained 70.18 % of As.

The nucleation and growth of aresnic sulphides from aqueous solutions was investigated by Bening using energy-dispersive X-ray experiments.[7] The synchrotron-based experiments showed that amorphous $As_2S_3$ crystallize to a mixture of amorphous $As_2S_3$ and realgar, or a mixture of orpiment and realgar, or to orpiment. XRD and EDS analyses showed that the end-product was not always monomineralic, *i.e.*, that the transformation reactions did not always go to completion. Complete transformation is dependent on (a) the starting material, (b) the temperature, (c) the redox conditions and (d) the ionic strength of the solution in equilibrium with the amorphous colloid.

Reaction path modeling was investigated by Claverlay *et al.* in the As–S system.[8] The object of this investigation was zonal mineral precipitation of As sulphide and As transport in an active geothermal field. Features relative to natural genesis were revealed as well as the synthesis of arsenic sulfides. The mechanism of oxidation of the most important compounds in As–S system were also presented.[7]

The present research consists of a kinetic study of the isothermal and non-isothermal oxidation of synthesized realgar. The main aim was to determine the kinetic parameters, as well as the mechanism of $As_2S_2$ oxidation.

## EXPERIMENTAL

A sample of synthesized $As_2S_2$, from the University "Paisiy Hilendarsky" Plovdiv (Bulgaria), of the following composition: 67.22 % As and 32.78 % S was used in the investigation. X-Ray analysis was performed in order to characterize the starting sample. The phase composition was determined using a Siemens X-ray diffractometer with a Cu anticathode and Ni filter at a voltage 40 kV and current of 18 mA. ICP–AES Analyses, using an Atomic Emission Spectrometer (model Plasma Vision 3410+ARL), were used to ascertain the purity of the starting sample. Analyses, including energy dispersive X-ray fluorescence (EDXRF) coupled with ICP–AES, were used to determine the composition of the samples after oxidative heating. Energy Dispersion X-ray Fluorescence analysis was done on Canberra equipment with the radioisotopes: Cd-109 (22.1 keV) and Am-241 (59.5 keV).

The non-isothermal oxidation process was investigated using the results of simultaneous DTA–TG–DTG analysis. A thermal analysis Derivatograph 1500 (MOM Budapest) was used, operating under the following conditions: air atmosphere, heating rate of 20 ºC/min and $T_{max}$ = 1273 K. Isothermal investigations were performed using standard equipment for isothermal investigations. The investigated sample was heated in a Mars furnace under isothermal conditions. A defined amount of air was introduced into the reaction area, while the generated gaseous reaction products were passed through absorption tanks filled with an aqueous solution of hydrogen peroxide, whereby sulfuric acid was produced. The gaseous arsenic compounds ($As_4O_6$) were removed from the gas stream in a spiral condenser located in front of the absorption tanks were $As_4O_6$ (g) was transformed into $As_2O_3$ (s). The produced sulfuric acid, was titrated against a standard solution sodium hydroxide, in the presence of an indicator to determine the of sulfur content, as well as the degree of desulphurization occuring during oxidative thermal treatment.

Amount of sulfur reacted with oxygen during process of oxidative roasting was colculated using equation:

$$\%S = \frac{V_{NaOH}N_{NaOH}E_s}{1000}\frac{100}{m} \tag{1}$$

where: $E_s$ – sulfur equivalent; $m$ – mass of the sample; $V_{NaOH}$ – volume of NaOH spent during titration,

and $N_{\text{NaOH}}$ – NaOH normality.

Degree of desulphurization was calculated using equation:

$$\%D = \frac{\%S}{S_1}\,100 \tag{2}$$

where: %$S$ – amount of sulfur reacted with oxygen during process of oxidative roasting, calculated using equation (1); $S_1$ – amount of sulfur present in starting sample (%).

Degree of desulphurisation calculated using Eq. (2) was used for determination of the kinetic parameters of oxidation, using Sharp's isothermal model, described later.

## RESULTS AND DISCUSSION

### Stoichiometry

The results of the X-ray analysis of the starting sample are presented in Fig. 1.

The first peak of the difractogram (X-ray), Fig. 1, is in the area characteristic for mineral realgar,[8] but the width of the peaks is an indication of an amorphous rather than a crystalline structure. The results presented in Fig. 1 are similar to the results presented in the literature,[6] and it can be stated that the transformation of amorphous As$_2$S$_2$ to crystalline realgar had already commenced during the synthesis of the starting As$_2$S$_2$ sample.
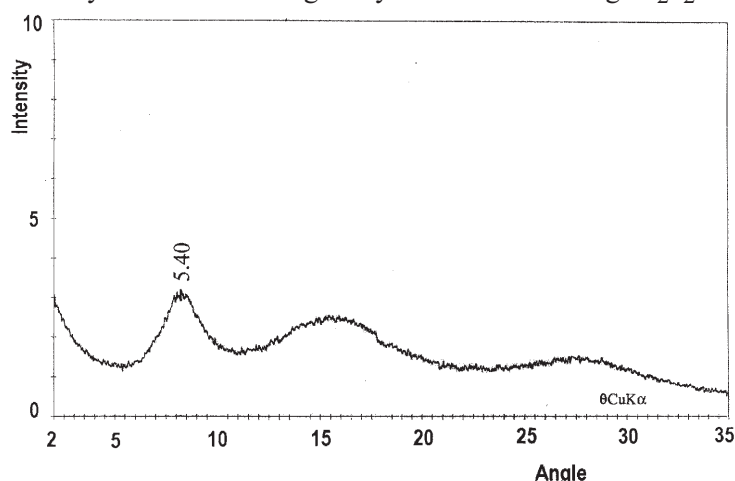


Fig. 1. X-Ray difratogram of the starting As$_2$S$_2$ sample.

The results of the thermal analysis, including DTA–TG–DTG, of the investigated realgar sample are presented in Fig. 2.

The DTA results show the existence of a first exothermal peak in the temperature range 150 – 320 ºC and second one at 320 – 670 ºC, both peaks are accompanied by mass loss, as seen in the TG curve, Fig. 2.

The results of ICP–AES analysis of the starting and As$_2$S$_2$ sample heated at 350 ºC are presented in Table I.

The results presented in Table I show that the starting sample contained 67.22 % As, which is in the stoichiometry range of As$_2$S$_2$. The sample of As$_2$S$_2$ heated at 350 ºC in
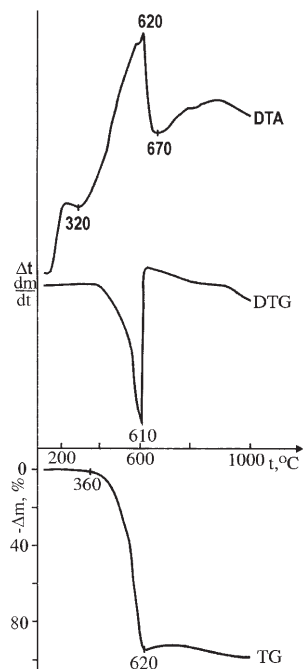
Fig. 2. DTA–TG–DTG Analysis of the $As_2S_2$ sample, heating rate 20 °C/min.

an air atmosphere contains 79.56 % As, which is in stoichiometry range of $As_4S_3$.

TABLE I. Results of ICP–AES analysis

| Sample | As/%-mas |
|---|---|
| 1) $As_2S_2$ Starting sample | 67.22 |
| 2) $As_2S_2$ Heated at 350 ºC | 79.56 |

Using calculations and comparison of the peak surfaces obtained by EDXRF analysis of the starting sample and of the sample heated at 350 ºC, the stoichiometry of the compound obtained after heating $As_2S_2$ at 350 ºC was calculated to be equal to $As_4S_{2.83}$, which agrees well with the results of ICP–AES analysis.

According to the presented analysis and literature data for the investigated process, the following mechanism can be proposed for the oxidation of $As_2S_2$:

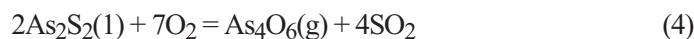Oxidation by air oxygen occurs, as heat is applied, according to the reaction[10,11]:

$$2As_2S_2 + 7O_2 = 2As_2O_3 + 4SO_2 \qquad (1)$$

Above 193 ºC, $As_2O_3$ sublimes[4] hence further oxidation occurs according to:

$$2As_2S_2 + 7O_2 = 2As_4O_6(g) + 4SO_2 \qquad (2)$$

Up to 315 ºC, parallel with reaction (2), the following reaction is possible:

$$2As_2S_2 + 9O_2 = 2As_2O_5 + 4SO_2 \qquad (3)$$

Above 321 ºC, the oxidation occurs according to:[12]

$$2As_2S_2(1) + 7O_2 = As_4O_6(g) + 4SO_2 \tag{4}$$

The introduced reaction mechanism is in agreement with the experimental results obtained by TG–DTG–DTA analysis. The mass loss seen on the TG curve is not significant until 360 ºC, after which the rate of mass loss increases significantly substantially larger intensity. The molar mass of the As$_2$S$_2$ is similar to those of As$_2$O$_3$ and As$_2$O$_5$, and as the amount of starting compound As$_2$S$_2$, reaching in the temperature interval up to the 360 ºC is small, the mass loss seen on the TG curve is small.

With further temperature increase, the solubility of sulphur decreases, hence, according to literature data, an equilibrium of As$_4$S$_3$ and gaseous sulphur in the melt exists at 445 ºC,[17] which can be presented by the reaction:

$$2As_2S_2(1) = 2As_4S_3(g) + 1/2\ S_2(g) \tag{5}$$

The formed gaseous sulphur reacts with air oxygen according to:

$$1/2\ S_2(g) + O_2(g) = SO_2(g) \tag{6}$$

The sum reaction is:

$$2As_2S_2(1) + O_2(g) = As_4S_3(1) + SO_2(g) \tag{7}$$
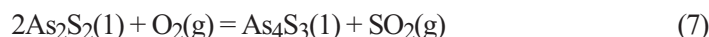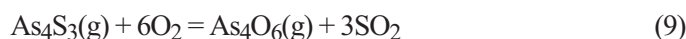
Nevertheless, ICP–AES and EDXRF results for the sample heated at 350 ºC show a composition adequate to the compound As$_4$S$_3$. According to this, it can be concluded that, under the employed experimental conditions, the transformation defined by reaction (5) is shifted towards lower temperatures.

The formed melt of As$_4$S$_3$ also reacts with oxygen:

$$As_4S_3(1) + 6O_2 = As_4O_6(g) + 3SO_2 \tag{8}$$
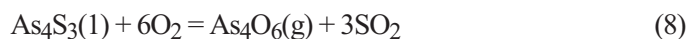
Above 534 ºC, parallel with reaction (8), the folowing reaction occurs:[11]

$$As_4S_3(g) + 6O_2 = As_4O_6(g) + 3SO_2 \tag{9}$$

Above 650 ºC, only reaction (9) can occur.

The first significant exothermal peak on the DTA curve is present in the temperature range of 150–320 ºC, where the oxidation is described by the reactions (1), (2) and (3). The endothermal process of As$_2$O$_3$ sublimation starts at 193 ºC but considering that the process is carried out under an oxidative atmosphere, it can be described by reaction (1), which gives reaction (2) when summed with the reaction:

$$2As_2S_3 = As_4O_6(g) \tag{10}$$

Thus, the endothermal reaction (10) is masked by the exothermal peak of reaction (2), which is why is not visible on the DTA curve as a separate entity.

A significant mass loss on the TG curve, Fig. 2, is registered after 360 ºC, because As$_2$O$_5$ is not stable in this temperature regime, dissociating at 315 ºC.[4] Accordingly, after 315 ºC, there are no solid reaction products in the system, the only product is gaseous As$_4$O$_6$.

An even substantial mass loss (almost linear) on the TG curve is registered above 534 ºC because this is when the formed $As_4S_3$ starts to evaporate. Now the reactants are also in gaseous form. Evaporation of $As_4S_3$ occurs through the temperature interval of 534–650 ºC.[11]

Oxidation in second temperatrue interval of 320–670 ºC is represented by the second exothermal peak on the DTA curve, which describes Eqs. (4)–(9).

The slight mass increase at temperatures above 620 ºC can only be explained by the formation of larger amount of gaseous reaction products which have to diffuse through the layer of the remaining liquid $As_4S_3$, where they become partially trapped in the form of included bubbles, which leads to some mass increase. Only after all the remaining liquid phase has evaporated is there complete mass loss registered on the TG curve.

According to the deduced mechanism, it can be concluded that process of $As_2S_2$ oxidation can be presented by two stages. The first stage is the melting of the $As_2S_2$ and its transformation to $As_4S_3$, with a small amount of the $As_2S_2$ being oxidized to $As_4O_6$ and $As_2O_5$, which occurs in the temperature interval 150–450 ºC, according to the DTA curve. The second stage occurs in the temperature interval 400–670 ºC and can be described as the oxidation of the formed $As_4S_3$ to $As_2O_6(g)$.

*Kinetics*

According to the character of the investigated process in the As–S–O system, which results in the coresponding shape of the DTA–TG–DTG curves, Fig. 2, it is possible, using the non-isothermal model of Borchardt and Daniels,[12] to determine the activation energy of oxidation, in the temperature range 320–670 ºC.

Using equation $k_i = \Delta T_i/A - a_i$, which is the essence of the Borchardt and Daniels model (where $A$ is the area of the peak present on the DTA–TG–DTG curve, $a_i$ – the
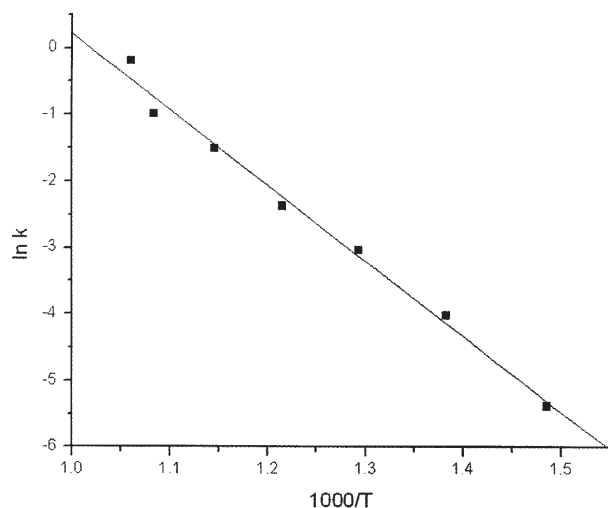


Fig. 3. Arrhenius diagram for the process of $As_2S_2$ oxidation obtained under non-isothermal conditions in the temperature interval 320–670 ºC.

areas of the peaks segments and $\Delta T_i$ – the temperature interval of the segments the rate constants $k_i$ were determined for different temperature intervals. According to this data, an Arrhenius diagram was constructed, Fig. 3.

Using the diagram in Fig. 3, the activation energy was calculated and found to be 95 kJ/mol, which is in the kinetic domain according to classical kinetic theory.[13,14]
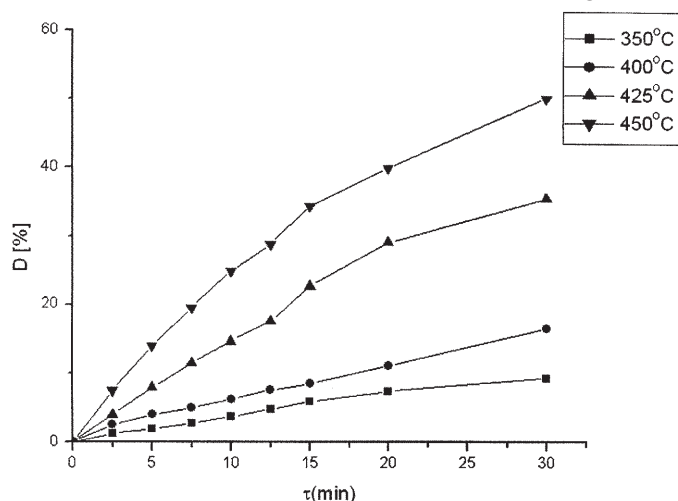


Fig. 4. Effect of temperature on the heating of As₂S₂.
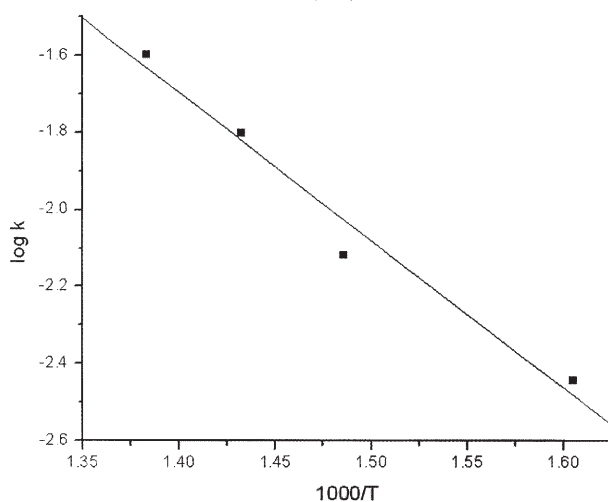


Fig. 5. Arrhenius diagram for the process of As₂S₂ oxidation obtained under isothermal conditions for temperature interval 350–450 ºC.

Also, the kinetic parameters of oxidation were calculated using the isothermal model, for the temperature interval 350–450 ºC. The results of the isothermal heating of the starting As₂S₂ samples in an air atmosphere are presented in Fig. 4, where $D$ is the degree of desulfurisation.

The selection of the kinetic model for the linearization of the experimental isotherms was done using the Sharp method of reduced half time of reaction.[15] The values of the reduced half time of reaction for the experimental data were approximated to values that represent the kinetic function $F_1$, for all three investigated compounds,

which means that the kinetic function for the linearization of the experimental results should be $F_1 = (-\ln(1-\alpha) = kt)$, according to the Sharp method, where: $\alpha$ is the extent of reaction, $k$ – the rate constant and $t$ – time.

The Arrhenius diagram of the rate constants, Fig. 5, constructed using the results from Fig. 4 and the equation for $F_1$, indicates a value of 73 kJ/mol for the activation energy, which is consistent with chemical reaction control.[13,14]

## CONCLUSIONS

(1) The mechanism of $As_2S_2$ oxidation is:

I stage of oxidation:

• Up to 193 ºC oxidation of $As_2S_2$ to $As_2O_3$ and $As_2O_5$

• At 193 ºC $As_2O_3$ sublimation to $As_4O_6(g)$

• At 315 ºC dissociation of $As_2O_5$ to $As_4O_6(g)$ and $O_2(g)$

• At 321 ºC $As_2S_2$ melting

• With further temperature increase, the solubility of surphur decreases, hence at 445 ºC, there is $As_4S_3$ and gaseous sulphur are in equilibrium in the melt.[8]

II Stage of oxidation

• Oxidation of $As_4S_3$ (1) to $As_4O_6(g)$

• In the temperature interval 534 – 650 ºC, $As_4S_3$ evaporation

• Oxidation in the gas phase.

(2) The reaction rates are fast and are chemically controlled with an activation energy of 95 kJ/mol, obtained under non-isothermal conditions in the temperature range 320–670 ºC, which covers the second stage of oxidation, and 75 kJ/mol, obtained under isothermal conditions in the temperature range 350 – 450 ºC, which covers the transformation of $As_2S_2$ into $As_4S_3$.

(3) The kinetic equation determined by the Sharp isothermal model is:

$$-\ln(1-\alpha) = 4.56 \times 10^3 \times e^{(-8780/T)} \times t$$

ИЗВОД

КИНЕТИКА И МЕХАНИЗАМ ПРОЦЕСА ОСКИДАЦИЈЕ ЈЕДИЊЕЊА $As_2S_2$

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У овом раду представљена су истраживања кинетике процеса оксидације једињења реалгара ($As_2S_2$) у изотермским и неизотермским условима. Добијене вредности енергије активације указују да се процес одвија у кинетичкој области при чему се честице реалгара оксидишу до $As_2O_3$ и $As_4O_6(g)$. Кинетичка једначина која најбоље описује посматрани процес је: $-\ln(1-\alpha) = 4.56 \times 10^3 \times e^{(-8780/T)} \times t$. У раду је предложен реакциони механизам и презентовани су резултати ICP–AES, EDXTF и термалне анализе.

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