ISSN 0020-1685, Inorganic Materials, 2018, Vol. 54, No. 7, pp. 621–626. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © A.V. Nitsenko, S.A. Trebukhov, A.K. Kasymzhanova, N.M. Burabaeva, 2018, published in Neorganicheskie Materialy, 2018, Vol. 54, No. 7, pp. 655–661.

Decomposition of a Synthetic Copper Sulfoarsenide

A. V. Nitsenko[a, *], **S. A. Trebukhov**[a], **A. K. Kasymzhanova**[a], **and N. M. Burabaeva**[a]
[a] *Institute of Metallurgy and Ore Beneficiation, Shevchenko str. 29/133, Almaty, 050010 Kazakhstan*
**e-mail: alina.nitsenko@gmail.com*

Received May 22, 2017; in final form, November 9, 2017

Abstract—We have studied the thermal behavior of synthetic lautite, a copper sulfoarsenide widespread in nature. The material was characterized by thermogravimetric analysis under nonisothermal and isothermal conditions. Using the data thus obtained, equations of nonisothermal formal kinetics, and the Kazeev–Erofeev–Kolmogorov equation with the Sakovich correction, we assessed kinetic parameters. Lautite decomposition to copper sulfides has been shown to be accompanied by the formation of tennantite as an intermediate phase. The sublimates consist of an alloy of arsenic sulfides. The E_a values obtained under nonisothermal conditions suggest that synthetic CuAsS dissociation is a kinetically controlled process. The E_a values obtained under isothermal conditions suggest that, at a temperature of 500°C, the lautite decomposition process switches from intermediate to diffusion control.

Keywords: kinetic parameters, lautite, arsenic, reduced pressure, dearsenation

DOI: 10.1134/S0020168518070105

INTRODUCTION

A considerable part of the world reserves of raw materials is accounted for by arsenic–polymetallic deposits [1–4], where arsenic is typically present in the form of sulfoarsenides, which pass into concentrate in the course of ore beneficiation and then, if there is no preliminary dearsenation step, become distributed over all metallurgical processing products, degrading their quality and the working environment. However, despite the large number of proposed technologies, research aimed at creating new and improving existing approaches to the processing of arsenic-containing raw materials remains a topical issue [5–9]. Because of this, the creation of physicochemical foundations in general and investigation of the mechanisms and general aspects of the decomposition of compounds characteristic of raw materials in particular are of scientific interest for designing technologies and supplementing reference data.

Along with tennantite ($Cu_{12}As_4S_{13}$) and enargite (Cu_3AsS_4), lautite (CuAsS) is one of the most widespread compounds in the composition of copper arsenic ores and concentrates.

Analysis of the available scientific and technological literature indicates that the thermal stability of arsenical copper compounds, such as $Cu_6As_4S_9$, $Cu_4As_2S_5$, Cu_3AsS_8, and $Cu_{12}As_4S_{13}$, in a neutral atmosphere at reduced pressures has been studied rather well [10–12]. There also data on the thermal behavior of copper arsenides [13]. At the same time, we found no data on the thermal behavior of CuAsS at normal or reduced pressures. Studies of lautite were concerned primarily with its crystal-chemical parameters [14–16].

The purpose of this work was to study the behavior of synthetic lautite at a reduced pressure.

EXPERIMENTAL AND CALCULATIONAL APPROACH

Synthetic copper sulfoarsenide was prepared by sintering a stoichiometric elemental mixture in evacuated silica ampules. X-ray diffraction characterization showed that the material contained 98.2% lautite.

Thermogravimetric analysis was carried out in a vertical vacuum system which ensured constant weighing of the sample. The system comprised a Nabertherm electric furnace with a B-180 controller, a quartz reactor (in which a spring balance was mounted), a KM-8 katharometer, and a 2NVR-5DM vacuum pump. The temperature in the reaction zone was measured by a Chromel–Alumel thermocouple (DTPK021-1.2/0.7 thermoelectric converter) with a TRM-1 single-channel microprocessor-controlled meter/controller. The pressure was measured by a McLeod gage and M110 aneroid barometer. Substances were weighed on an Ohaus-Pioneer analytical balance.

The phase composition of the samples was determined by X-ray diffraction on a D8 Advance diffractometer (Bruker, Germany).

Our experiments were carried out under nonisothermal conditions in the temperature range 24–

1000°C at pressures of 0.2, 0.133, 0.665, 1.33, and 91.77 kPa (heating rate of 5–6°C/min) and under isothermal conditions: at 400, 450, 500, 550, and 600°C and a pressure of 0.133 kPa. The sample weight was 0.5 g, and the particle size was 0.05–0.063 mm.

Mathematical processing of the data obtained under nonisothermal conditions was performed using equations of nonisothermal formal kinetics. As a starting equation, we used the Arrhenius law, which allows one to determine the reaction rate constant (k_n), reaction order (n), and apparent activation energy (E_a).

Under the assumption that the decomposition rate is proportional to the amount of unreacted substance to some power n, the decomposition process can be described by the differential equation [17]

$$dm/d\tau = k_n (m_0 - m_r)^n \exp(-E_a/RT), \qquad (1)$$

where $dm/d\tau = v$ is the decomposition rate measured in any units, m_0 (mg) is the initial mass of the substance, m_r (mg) is the mass of the substance that entered into the reaction, R is the gas constant, and T (K) is the absolute temperature.

Because of the vaporization (sublimation) of volatile components, the mass of the substance that entered into the reaction is related to the initial mass by

$$m_r = m_0 m_v / m_{\max}, \qquad (2)$$

where m_v and $m_{\max}$ (mg) are the current and maximum possible masses of the vaporized substance.

To find kinetic parameters, it is necessary to know m_0, m_v, and $m_{\max}$ for each decomposition step, which adds complexity to calculations. The use of the degree of decomposition, α, relative to the initial amount of the substance, m_0, simplifies calculations. Equation (1) then takes the form

$$v = k_n (\alpha_{\max} - \alpha)^n \exp(-E_a/RT), \qquad (3)$$

where $\alpha_{\max}$ (%) is the maximum possible degree of decomposition and α (%) is the actual degree of decomposition.

After a transformation, Eq. (3) takes a form convenient for calculating kinetic parameters:

$$\ln\left[v/(\alpha_{\max} - \alpha)^n\right] = -E_a/RT + \ln k_n = -A/T + B. \qquad (4)$$

It is known that, in the case of the release of volatile components, the reaction rate is determined by various factors, basic among which are heat delivery conditions and diffusion across the layer. Note that the heat delivery area is proportional to the residual mass or varies more slowly and that the growth of an inert component layer hinders both the diffusion process and heat delivery.

In view of this, the most likely reaction order for thermal decomposition at a reduced pressure is ≤1. This assumption is supported by the following: In vacuum the vaporization rate depends only on the slowly varying geometric vaporization surface facing the vapor phase; that is, the reaction order is near zero. The thermal decomposition of substances is in most cases a heterogeneous topochemical transformation which follows rate laws for first-order reactions. The reason for this is that the rate of a solid-state reaction is determined by diffusion of the reactants across the layer of the reaction products [18].

If the values obtained by processing experimental data using a first-order or near-first-order equation are inconsistent with a linear dependence, or a considerable value of n is needed for linearizing a curve, this points to a change in the nature of the process, for example, to an effect of diffusion factors in this region or the formation of intermediate compounds that decompose at a different rate.

The maximum possible degree of decomposition can be evaluated both by calculations and in experiments. In this study, the maximum achievable degree of decomposition was taken to be that at which all volatile components are in the vapor phase.

To find kinetic constants of the lautite decomposition process under isothermal conditions, we utilized the Kazeev–Erofeev–Kolmogorov equation, which is most often used and adequately describes the kinetics of topochemical reactions [19–22]:

$$\alpha = 1 - e^{-k\tau^n}, \qquad (5)$$

where α (%) is the degree of decomposition, the coefficient k characterizes the rate constant, and n is the exponent of the time parameter.

The decomposition rate constant (K_C) was calculated using the Sakovich correction [23]:

$$K_C = nk^{1/n}. \qquad (6)$$

RESULTS AND DISCUSSION

It is known from the literature that, at normal pressure, CuAsS melts peritectically and decomposes into arsenic and a melt at 596°C or, possibly, $Cu_{12+x}As_{4+y}S_{13}$, arsenic, and melt at 574°C [24]. Rikel et al. [25] assumed that, at a temperature of 574°C, lautite decomposes into tennantite and arsenic and that, at 596°C, the tennantite formed further decomposes to give copper sulfides.

The results of experiments carried out under nonisothermal conditions (Fig. 1) demonstrate that, at normal pressure, lautite begins to decompose at a temperature of ≈445°C, which is accompanied by a weight loss due to the sublimation of volatile components. At a temperature of ≈525°C, the rate of weight loss increases sharply. Starting at this temperature, the sublimate consists of arsenic sulfide compounds (As_2S_3 and As_4S_4). After the peak at a temperature of ≈575°C, the rate of lautite decomposition falls off, and then rises again at 725°C due to the decomposition of

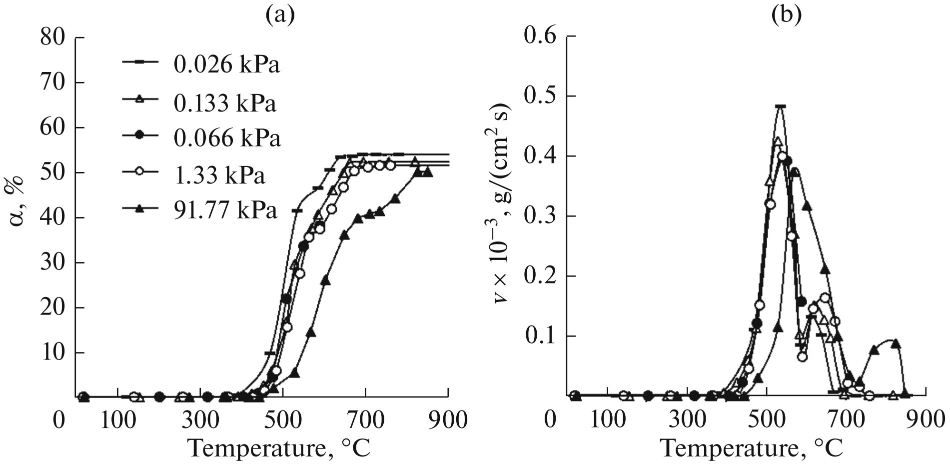

Fig. 1. (a) Degree and (b) rate of CuAsS decomposition under isobaric–nonisothermal conditions at different pressures.

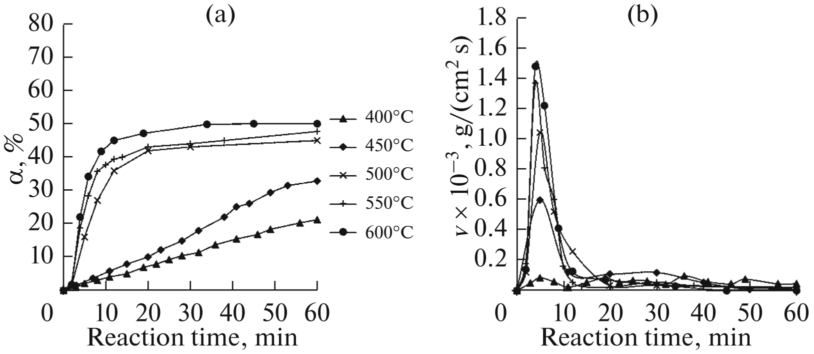

Fig. 2. (a) Degree and (b) rate of CuAsS decomposition at a pressure of 0.133 kPa and different constant temperatures.

the tennantite (formed as a result of lautite decomposition) to an alloy of copper sulfides ($Cu_{2-x}S$). At a reduced pressure (0.0266–1.33 kPa), all of the main points indicated above shift to lower temperatures by about 100°C.

The results of experiments carried out under isothermal conditions are presented in Fig. 2. Here, a relatively high degree of lautite decomposition can be reached at temperatures above 500°C. It is worth noting that lautite decomposes at lower temperatures as well, but at a slower rate, so that a longer time is needed for CuAsS decomposition to nontoxic phases in the residue.

Figure 3 presents results of data processing using the equation of nonisothermal formal kinetics (4). We kinetically analyzed the portion of the curves corresponding to the increase in the rate of CuAsS decomposition to its maximum level. It is seen that, in the temperature range where lautite decomposes to tennantite, the experimental data represented as a plot of $\log v$ against $1/T$ show linear behavior, suggesting that the equation chosen is well suited for assessing kinetic parameters.

Table 1 lists the coefficients A and B in the Arrhenius equation (4) obtained in this study and the kinetic parameters calculated from them for the process of lautite decomposition under isobaric–nonisothermal conditions (first-order reaction). As seen from Table 1, the apparent activation energy varies rather little over the entire pressure range studied. The E_a value found suggests that synthetic CuAsS dissociation is a kinetically controlled process.

Figure 4 and Table 2 present results of isobaric–isothermal experimental data processing using the Kazeev–Erofeev–Kolmogorov equation (5). A satisfactory arrangement of data points ($r = 0.9$) suggests that this equation is well suited for assessing kinetic parameters of lautite decomposition. It is seen from the calculation results that the CuAsS decomposition process is a first-order reaction.

The activation energy for lautite decomposition was assessed from the linear dependence of the rate constant for copper arsenide decomposition (Fig. 5).

The dependence has two linear portions with a break near the point corresponding to 500°C, which can be interpreted as evidence of a change in the

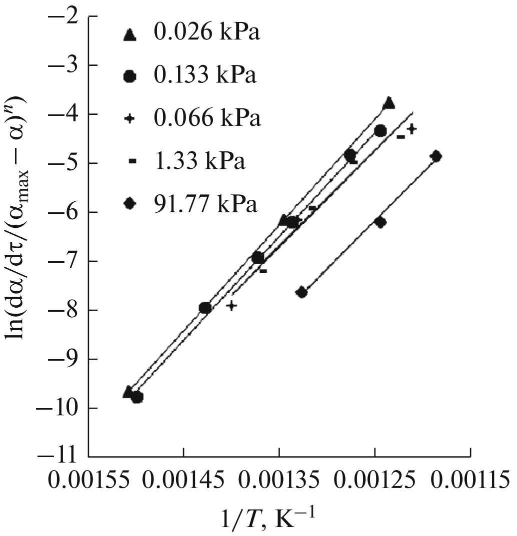

Fig. 3. Temperature dependences of the decomposition rate for lautite at different pressures.

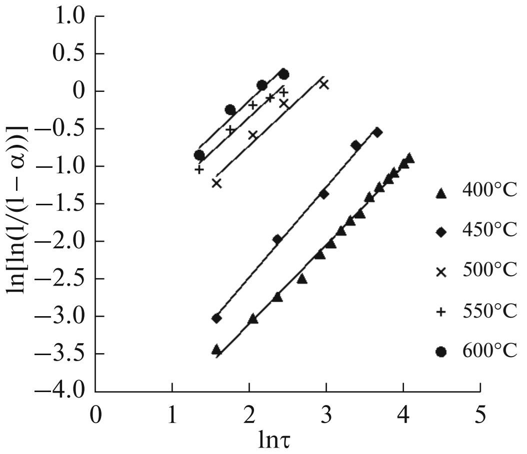

Fig. 4. Time dependences of the decomposition rate for lautite at a pressure of 0.133 kPa and different constant temperatures.

mechanism of the decomposition process, which probably follows the scheme

$$\mathrm{CuAsS} \xrightarrow{345\text{–}445°\mathrm{C}} \mathrm{Cu_{12}As_4S_{13}} + \mathrm{As_2S_3}\uparrow + \mathrm{As_4S_4}\uparrow \qquad (7)$$
$$\xrightarrow{595\text{–}725°\mathrm{C}} \mathrm{Cu_2S} + \mathrm{As_2S_3}\uparrow + \mathrm{As_4S_4}\uparrow .$$

That the decomposition process follows this scheme is evidenced by X-ray diffraction characterization results for the CuAsS decomposition products obtained in isothermal experiments under the following conditions: temperature, 400–600°C; pressure, 0.133 kPa; holding time, 20 min (Fig. 6).

The calculated apparent activation energies in the temperature ranges 400–500 (segment *A*–*B*) and 500–600°C (segment *B*–*C*) are 88.86 and 35.58 kJ/mol, respectively.

In comparing the E_a values obtained, it should be taken into account that the E_a for the decomposition of the compound under nonisothermal conditions was assessed using only experimental data for the CuAsS decomposition step, where the effect of diffusion factors was rather weak, whereas in the case of isothermal conditions we used data for both CuAsS and its decomposition product $\mathrm{Cu_{12}As_4S_{13}}$.

Table 1. Kinetic parameters of lautite decomposition under nonisothermal conditions

p, kPa	T, K	α, %	Coefficients of the equation $\log[d\alpha/d\tau/(\alpha_{\max}-\alpha)^n] = -A/T + B$		E_a, kJ/mol	$k_n \times 10^{-9}$, s^{-1}	$k_0 \times 10^{-12}$, s^{-1}	r^2
			A	B				
0.026	663–809	0.29–41.40	−21558	22.851	179.147	8.517	3.023	1
0.133	667–803	0.11–29.41	−21142	22.074	175.690	3.914	0.842	0.99
0.666	714–825	0.81–33.53	−19599	19.770	162.868	0.390	0.016	0.95
1.33	730–815	1.35–27.45	−19369	19.483	160.956	0.293	0.005	0.97
91.77	753–842	2.1–14.47	−19613	18.348	162.984	0.094	0.001	0.99

Table 2. Kinetic parameters of lautite decomposition under isobaric–isothermal conditions (pressure of 0.133 kPa)

t, °C	$1/T$, K^{-1}	n	$\ln k$	r^2	$\ln K_C$	$\log K_C$	K_C, min^{-1}
400	0.00149	1.0612	−5.2421	0.99	−4.8804	−2.1191	0.00529
450	0.00138	1.2108	−4.9306	0.99	−3.8809	−1.6852	0.00722
500	0.00129	0.9567	−2.657	0.95	−2.8215	−1.2252	0.07016
550	0.00122	0.9526	−2.2768	0.95	−2.4387	−1.0589	0.10261
600	0.00115	0.971	−2.0972	0.95	−2.1893	−0.9506	0.1228

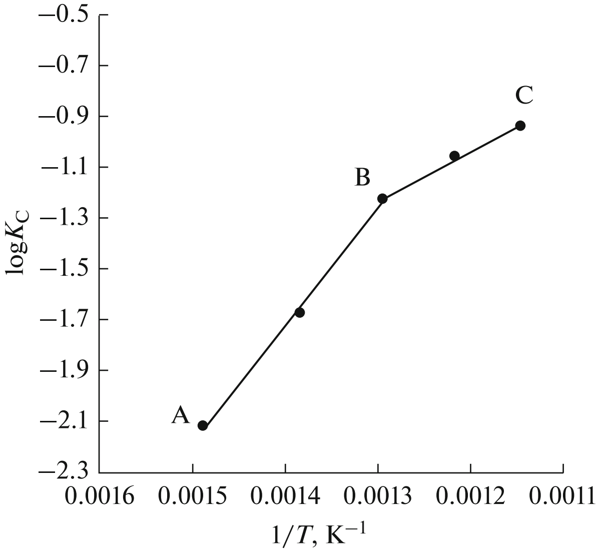

Fig. 5. Arrhenius plot of the decomposition rate constant for CuAsS at a pressure of 0.133 Pa.

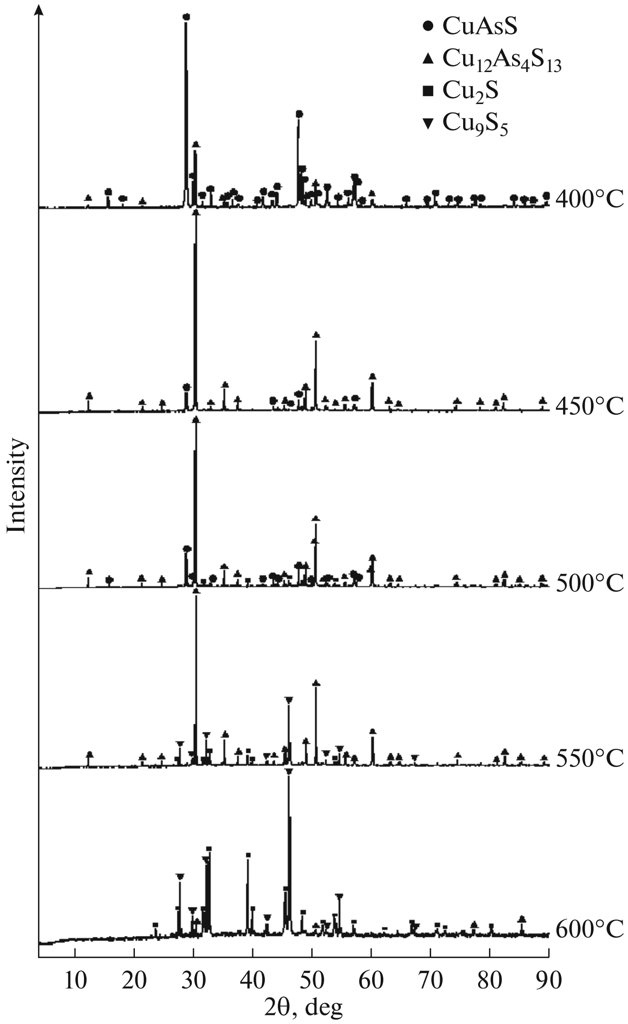

Fig. 6. X-ray diffraction patterns of the product of CuAsS decomposition (residue) at different temperatures.

CONCLUSIONS

The present results lead us to the following conclusions:

In the pressure range 0.0266–91.77 kPa at a constantly varying temperature, a synthetic analog of the natural compound CuAsS (lautite) decomposes in two steps according to the scheme

$$CuAsS \xrightarrow{345-445°C} Cu_{12}As_4S_{13} + As_2S_3\uparrow + As_4S_4\uparrow \xrightarrow{595-725°C} Cu_2S + As_2S_3\uparrow + As_4S_4\uparrow.$$

The apparent activation energy evaluated using nonisothermal kinetics methods for CuAsS decomposition rises with decreasing residual pressure in the system: from 162.98 kJ/mol at a pressure of 91.77 kPa to 179.15 kJ/mol at a pressure of 0.026 kPa. The rate constant of the decomposition reaction also increases: from 0.001×10^{-12} to 3.023×10^{-12} s^{-1}.

Under isobaric–isothermal conditions, at temperatures from 450 to 600°C, most volatile elements are removed during the first 10 min.

The apparent activation energies calculated by the Kazeev–Erofeev–Kolmogorov equation (88.86 and 35.58 kJ/mol) suggest that, at a temperature of 500°C, the lautite decomposition process switches from intermediate to diffusion control.

ACKNOWLEDGMENTS

This work was supported by the Kazakhstan Ministry of Education and Science, project no. 1293/GF4.

REFERENCES

1. *Kratkaya khimicheskaya entsiklopediya* (Concise Chemical Encyclopedia), Knunyants, I.L., Ed., Moscow: Sovetskaya Entsiklopediya, 1963, vol. 2, p. 995.
2. *Gornaya entsiklopediya* (Mining Encyclopedia), Kozlovskii, E.A., Ed., Moscow: Sovetskaya Entsiklopediya, 1984.
3. Rtskhiladze, V.G., *Mysh'yak* (Arsenic), Moscow: Metallurgiya, 1969.
4. Okhota, D.M., *Osnovy metallurgii* (Principles of Metallurgy), Moscow: *Metallurgiya*, 1968, vol. 5, p. 520.
5. Perederii, O.G. and Naboichenko, S.S., Calculation of a reactor for trivalent arsenic extraction via sulfide route, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.,* 2017, no. 3, pp. 31–36.
6. Kopylov, N.I., Kaminskii, Yu.D., and Moldurushku, R.O., Arsenic removal from a dump waste cake from the TUVAKOBAL'T integrated plant, *Khim. Tekhnol.,* 2009, vol. 10, no. 11, pp. 669–673.
7. Turygin, V.V., Smirnov, M.K., Smetanin, A.V., Zhukov, E.G., Fedorov, V.A., and Tomilov, A.P., Electrochemical arsenic extraction from nonferrous metals industry waste, *Inorg. Mater.,* 2008, vol. 44, no. 9, pp. 946–953.

8. Smetanin, A.V., Pyshkin, A.S., Osipov, G.N., Sokhadze, L.A., Smirnov, M.K., Turygin, V.V., Zhukov, E.G., Potolokov, V.N., Tomilov, A.P., and Fedorov, V.A., Arsenic extraction from nonferrous metals industry waste, *Inorg. Mater.,* 2007, vol. 43, no. 10, pp. 1219–1229.
9. Boboev, I.R., Strizhko, L.S., Bobozoda, Sh., and Gorbunov, E.P., Kinetic investigation of sulfidizing annealing of scorodite in processing of refractory oxidized gold-containing ores, *Russ. Metall.* (Engl. Transl.), 2016, no. 3, pp. 171–173.
10. Kuzgibekova, Kh., Mil'ke, E.G., Isabaev, S.M., and Polukarov, A.N., Thermoanalytical study of copper thioarsenates, *Kompleksn. Ispol'z. Miner. Syr'ya,* 1987, no. 8, pp. 57–61.
11. Abramov, A.S., Khrapunov, V.E., Isakova, R.A., Moldabaev, M., and Trebukhov, S.A., Decomposition rate of tennantite in vacuum, *Khim. Zh. Kazakhstana,* 2005, no. 2, pp. 29–37.
12. Isakova, R.A., Khrapunov, V.E., Abramov, A.S., Shendyapin, A.S., and Trebukhov, S.A., Dissociation pressure of tennantite, *Kompleksn. Ispol'z. Miner. Syr'ya,* 2005, no. 2, pp. 47–50.
13. Nitsenko, A.V., Abramov, A.S., Khrapunov, V.E., Moldabaev, M., and Isakova, R.A., Thermal decomposition of copper arsenide in vacuum, *Vestn. Nats. Akad. Nauk Respubl. Kazakhstan,* 2010, no. 3, pp. 52–55.
14. Weil, R. and Hocart, R., The crystal structure of lautite, *C. R. Seances Acad. Sci.,* 1939, no. 209, pp. 444–448.
15. Marumo, F. and Nowacki, W., The crystal structure of lautite and of sinnerite, a new mineral from the Lengenbach quarry, *Schweiz. Mineral. Petrog. Mitt.,* 1964, no. 44, pp. 439–454.
16. Bindi, L., Catelani, T., Chelazzi, L., and Bonazzi, P., Reinvestigation of the crystal structure of lautite, CuAsS, *Acta Crystallogr., Sect. E: Crystallogr. Commun.,* 2008, vol. 64, no. 3, pp. 22–26.
17. Wendlandt, W.W., *Thermal Methods of Analysis,* New York: Wiley, 1974.
18. Guseva, A.F., *Tverdofaznye reaktsii pri poluchenii i ekspluatatsii neorganicheskikh materialov* (Solid-State Reactions in the Preparation and Service of Inorganic Materials), Yekaterinburg: Ural. Univ., 2009.
19. Eremin, E.N., *Osnovy khimicheskoi kinetiki* (Principles of Chemical Kinetics), Moscow: Vysshaya Shkola, 1976.
20. Erofeev, B.V., Generalized equation of chemical kinetics with application to reactions involving solid substances, *Dokl. Akad. Nauk SSSR,* 1943, vol. 52, no. 6, pp. 515–518.
21. Kolmogorov, A.N., On the statistical theory of metal crystallization, *Izv. Akad. Nauk SSSR,* 1937, vol. 1, no. 3, pp. 355–359.
22. Kazeev, S.A., *Kinetika v prilozhenii k metallovedeniyu* (Kinetics with Application to Physical Metallurgy), Moscow: Oborongiz, 1956.
23. Sakovich, G.V., Concerning some equations for the kinetics of reactions involving solid substances in current use, *Uch. Zap. Tomsk. Gos. Univ.,* 1956, no. 26, p. 103.
24. Ronald Frost, B., Partial melting of sulfide ore deposits during medium and high-grade metamorphism, *Can. Mineral.*, 2002, vol. 40, pp. 1–18.
25. Rikel, M., Harmelin, M., and Prince, A., Arsenic–copper–sulfur, *Ternary Alloys,* 1994, vol. 11, pp. 109–127.

Translated by O. Tsarev