

Kh.B.Omarov, Z.B.Absat, S.K.Aldabergenova,
N.Zh.Rakhimzhanova, A.B.Karimova

*Ye.A.Buketov Karaganda State University
(E-mail: zaure.absat.76@mail.ru)*

The analysis of properties of arsenates and antimonates of barium based on diagrams of the partial pressures

By results of thermodynamic calculations diagrams the partial pressure of systems $Ba-O_2-SO_2-As_2$, $Ba-O_2-SO_2-Sb_2$ are constructed. The analysis of interactions of compounds of antimony and arsenic in systems $Ba-O_2-SO_2-As_2$, $Ba-O_2-SO_2-Sb_2$ is carried out at 25 °C and 1 atm. general pressure. Areas of stability of arsenate and arsenite of barium, and also antimonite and an antimonat of barium are defined.

Key words: thermodynamic analysis, arsenite, arsenate, antimonite, stability, antimonat, diagrams of the partial pressures.

One of the priority directions in the program of economic development of our state is the solution of the questions connected with recycling of the enterprises of nonferrous metallurgy in the form of finished products or forms, safe for environment. In particular, in production of copper there is a problem of a reduction of arsenic and antimony from a production cycle in the form of low-toxic and steady connections. At the existing schemes of processing, in the conditions demanding high complexity of use of raw materials, the products containing arsenic and antimony circulate as between the enterprises of various productions (lead, zinc, copper, etc.), and in separate factories between the main repartitions. It leads to accumulation of harmful impurity in turns and as a result — to disturbance of technology and losses of valuable metals, environmental pollution. The materials containing arsenic and antimony don't find wide application and go either to tailings dams, or to dumps, therefore a necessary condition of storage or burial is their resistance to influences of environment (oxygen, various oxidizers and reducers, water). Application in the this work of thermodynamic methods for consideration of stability of components and products of interactions in the systems containing arsenic and antimony, and also for the analysis, the forecast and optimization of carrying out chemical and technological processes, showed their theoretical importance in the solution of some practical tasks.

The thermodynamic analysis of interactions allows to comprehensively assess the nature of interactions in system and to predict behavior of connections, elements of system. Moreover, thermodynamic indicators give the chance to define safety of connections of system in relation to environment. This fact is especially important at utilization, burial of any waste, by-products of the enterprises.

Studying of physical and chemical, thermodynamic and kinetic parameters piro- and gidro-metallurgical processes allows to optimize and increase their efficiency.

Transfer to a solid phase of such undesirable impurity in copper electrolyte, as arsenic and antimony is the one of the main ways of their utilization in copper hydrometallurgy for the purpose of their further storage or burial. However in the conditions of caused by natural factors (water, air, influence of a sunlight, etc.), behavior of arsenic and antimony will be defined by a form of their existence.

If in the field of water existence stability of antimonat and arsenates of barium can be characterized by solubility, in oxidizing and recovery areas about behavior of arsenic and antimony information is practically absent.

In this work the analysis of systems $Ba-O_2-SO_2-As_2$, $Ba-O_2-SO_2-Sb_2$ with use of a method of construction of diagrams the partial pressures is submitted.

On the basis of diagrams the partial pressures possibly the solution of the questions connected with course of chemical reactions in systems, the direction of reactions and stability of the phases making them.

In the table 1 given the reactions of interaction of barium and its some connections, oxygen, oxide of sulfur (IV) and gaseous arsenic, Gibbs's energy of these reactions and value the partial pressures of O_2 , SO_2 , and As_2 in system $Ba-O_2-SO_2-As_2$ [1].

Table 1

**Partial pressures of O₂, SO₂ and As₂ of an equilibrium state of system
of Ba-O₂-SO₂-As₂ at 25 °C and 1 atm. general pressure**

№	Equation of reactions	$\Delta G_{\text{reaction}}^0$ kcal/mol	$\lg P_{O_2}$	$\lg P_{SO_2}$	$\lg P_{As}$
1	Ba+0,5O ₂ =BaO	-132,00	-193,53	—	—
2	BaO+0,5O ₂ =BaO ₂	-3,80	-5,57	—	—
3	Ba+SO ₂ =BaS+O ₂	-32,71	23,98	-23,98	—
4	BaO+SO ₂ =BaS+1,5O ₂	99,29	-48,52	72,79	—
5	BaO+SO ₂ +0,5O ₂ =BaSO ₄	-119,36	-173,54	-86,77	—
6	BaO ₂ +SO ₂ =BaSO ₄	-114,56	—	-83,98	—
7	BaS+2O ₂ =BaSO ₄	-217,65	-79,78	—	—
8	Ba+As ₂ +2O ₂ =Ba(AsO ₂) ₂	-435,36	-159,59	—	-319,18
9	BaO+As ₂ +1,5O ₂ =Ba(AsO ₂) ₂	-303,36	-148,27	—	-222,40
10	Ba ₃ (AsO ₄) ₂ +2As ₂ =3Ba(AsO ₂) ₂ -2O ₂	-550,40	-201,68	—	201,68
11	3BaO ₂ +As ₂ +O ₂ =Ba ₃ (AsO ₄) ₂	-348,5	-255,5	—	-255,5
12	BaS+As ₂ +3O ₂ =Ba(AsO ₂) ₂ +SO ₂	-402,65	—	294,3	-73,57

According to the calculated values (Table 1) the diagram the partial pressures of system Ba-O₂-SO₂-As₂ is constructed (Fig. 1). Lines *a*, *i* — the top and lower limits of stability of water. Numbers of lines on the diagram correspond to numbers of the chemical equations presented in Table 1 [2].

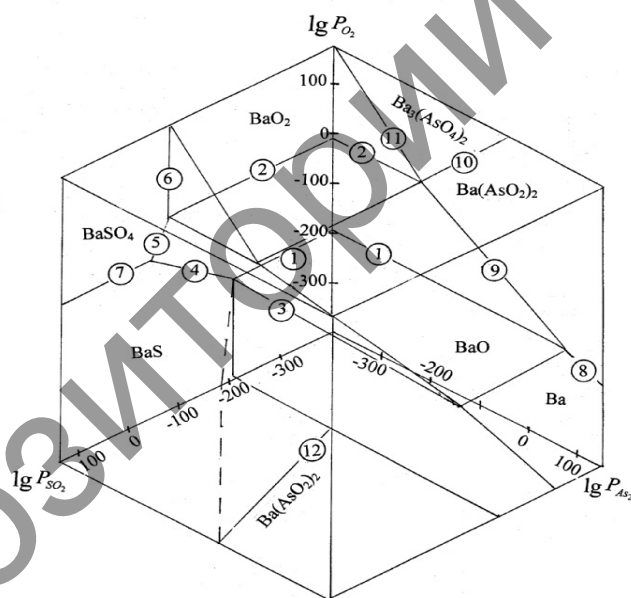


Figure 1. Diagram of the partial pressures of the system Ba-O₂-SO₂-As₂ at 25 °C and 1 atm. total pressure

Apparently from the diagram, metal barium can exist only at very low values of partial pressure of oxygen that is confirmed by its absence in nature in a free state.

According to the diagram in recovery area metal barium and its such connections as oxide (BaO) and arsenite of barium Ba(AsO₂)₂ is steady. At increase of partial pressure of oxygen barium oxide BaO in water area is oxidized to BaO₂ which is steadier in the oxidizing atmosphere. Barium arsenite on 10 reactions passes into barium arsenate. In recovery area there are also a sulfide of barium (BaS), barium arsenite (Ba(AsO₂)₂) and oxide of barium (BaO), however these connections can be and in the presence of water. According to reactions (1, 3, 8) interacting with oxygen, barium forms oxide of barium (BaO), with sulfur (IV) oxide — sulfide of barium (BaS), with gaseous arsenic — barium arsenite. Barium sulfide at higher values of partial pressure of oxygen passes on reaction 7 into sulfate of barium (BaSO₄) which is stable both in a water existence zone, and in oxidizing area.

Areas of stability of sulfide of barium and arsenite of barium are differentiated by reaction (12). The area of existence of sulfate of barium is limited to reactions (5,6,7). Barium oxide in the presence of oxygen passes into peroxide of barium (BaO_2) (2). At interaction with oxide of BaO sulfur (IV) forms sulfate of barium (4), with gaseous arsenic on reaction the 9th arsenite of barium $Ba(AsO_2)_2$ which in compliance (10) passes with reaction into barium orto-arsenate ($Ba_3(AsO_4)_2$).

Arsenate and arsenite of barium, as well as arsenical compounds of lead the stable connections having extensive zones of stability. Thus, the received results are according to literary data on thermal and chemical stability of arsenical compounds of barium [3].

In table 2 are given reactions of interaction of barium, its some connections, oxygen, oxide of sulfur (IV) and gaseous antimony, value of energy of Gibbs of reactions and the partial pressures of O_2 , SO_2 , and Sb_2 in $Ba-O_2-SO_2-Sb_2$ system.

Table 2

Partial pressures of O_2 , SO_2 , and Sb_2 of an equilibrium state of $Ba-O_2-SO_2-Sb_2$ system at 25 °C and 1 atm. general pressure

№	Equation of reactions	$\Delta G_{reaction}^0$, kcal/mol	$lg P_{O_2}$	$lg P_{SO_2}$	$lg P_{Sb_2}$
1	$Ba+0,5O_2=BaO$	-132,00	-193,53	-	-
2	$BaO+0,5O_2=BaO_2$	-3,80	-5,57	-	-
3	$Ba+SO_2=BaS+O_2$	-32,71	23,98	-23,98	-
4	$BaO+SO_2=BaS+1,5O_2$	99,29	-48,52	72,79	-
5	$BaO+SO_2+0,5O_2=BaSO_4$	-119,36	-173,54	-86,77	-
6	$BaO_2+SO_2=BaSO_4$	-114,56	-	-83,98	-
7	$BaS+O_2=BaSO_4$	-217,65	-79,78	-	-
8	$3Ba+Sb_2+4O_2=Ba_3(SbO_4)_2$	-861,55	-157,91	-	-631,63
9	$3BaO+2,5O_2+Sb_2=Ba_3(SbO_4)_2$	-465,55	-136,52	-	-341,31
10	$3Ba(SbO_2)_2=Ba_3(SbO_4)_2+2Sb_2+2O_2$	273,15	100,13	-	-100,13
11	$BaO+Sb_2+1,5O_2=Ba(SbO_2)_2$	-261,15	-127,64	-	-191,46
12	$BaO_2+Sb_2+O_2=Ba(SbO_2)_2$	-257,35	-188,67	-	-188,67
13	$3BaS+Sb_2+7O_2=Ba_3(SbO_4)_2+3SO_2$	-763,42	-	187,27	-70,22

On the calculated values (Table 2) the diagram the partial pressures of system $Ba-O_2-SO_2-Sb_2$ is constructed. This diagram describes areas of existence of such compounds of barium as oxide, sulfide, sulfate, orto-antimonat and piro-antimonat (Fig. 2).

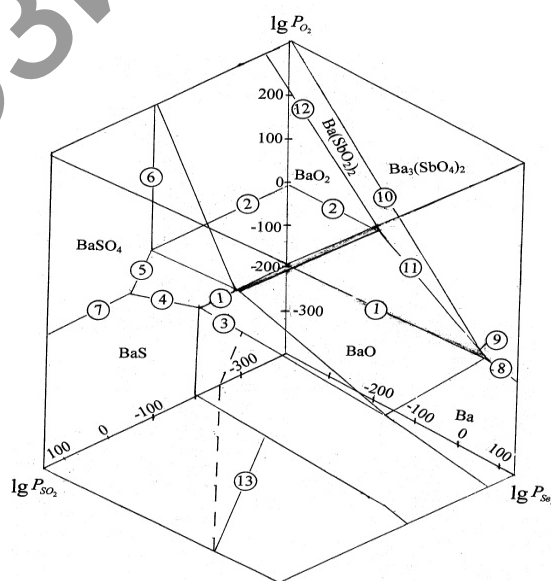


Figure 2. Diagram of the partial pressures of the system $Ba-O_2-SO_2-Sb_2$ at 25 °C and 1 atm. total pressure

According to drawing of 2 lines *a* and *b* — the top and lower limits of stability of water. Numbers of lines are showed on the diagram according to numbers of the chemical equations presented in Table 2.

In recovery area there is a dependence of an arrangement of metal barium, sulfide of barium and an antimonat and antimonite of barium on the partial pressure of oxygen. With increase of partial pressure of oxygen metal barium passes into BaO barium oxide (line 1), barium sulfide (reaction 3), antimonat of barium $Ba_3(SbO_4)_2$ (reaction 8) and antimonite of barium $Ba(AsO_2)_2$ which are steady also in the presence of water. At further increase in partial pressure of oxygen oxide of barium interacting with oxygen, forms barium peroxide BaO_2 (line 2), barium sulfide — barium sulfate (line 7). On 10 reactions antimonite of barium passes in antimonat of barium. It should be noted that in the field of existence of water are located: oxide, antimonite, antimonat, sulfate and sulfide of barium.

On the basis of this diagram it is possible to do a conclusion that antimonite and antimonat of barium $Ba(SbO_2)_2$ и $Ba_3(SbO_4)_2$ — stable connections in the oxidizing, recovery atmosphere, and also in the field of stability of water.

Comparison of diagrams of $Ba-O_2-SO_2-Sb_2$ и $Ba-O_2-SO_2-As_2$ systems showed that the volume occupied on the diagram by the barium arsenite, much more volume occupied by barium antimonite whereas arsenate of barium occupies smaller area of existence in comparison with barium antimonite.

Thus, the received results about stability of arsenite, arsenate and antimonite, an antimonat of barium confirm data of authors [4].

References

- 1 Касенов Б.К., Алдабергенов М.К., Пашилкин А.С. Термодинамические методы в химии и металлургии. — Алматы: Рауан, 1994. — 126 с.
- 2 Пашилкин А.С., Спивак М.М., Малкова А.С. Применение диаграмм парциальных давлений в металлургии. — М.: Металлургия, 1984. — 160 с.
- 3 Справочник химика / Под ред. Б.П.Никольского. — Л.: Наука, 1971. — Т. 3. — 1008 с.
- 4 Жамбеков М.И. Диаграммы парциальных давлений системы $Cu-As_2-S_2-O_2$ при 298,15 К // Абишевские чтения — 2011: Гетерогенные процессы в обогащении и металлургии. — Караганда, 2011. — С. 404–405.

Х.Б.Омаров, З.Б.Әбсәт, С.К.Алдабергенова, Н.Ж.Рахимжанова, А.Б.Каримова

Парциалды қысым диаграммалары негізінде арсенаттар мен антимоноаттардың қасиеттерін талдау

Мақалада термодинамикалық есептеулер нәтижесінде $Ba-O_2-SO_2-As_2$ және $Ba-O_2-SO_2-Sb_2$ жүйелерінің парциалды қысым диаграммалары құрылған. $Ba-O_2-SO_2-As_2$, $Ba-O_2-SO_2-Sb_2$ жүйелерінде 25 °С температурада және 1 атм. жалпы қысымдағы сурьма мен күшәла қосылыстарының әрекеттесуінің талдауы жүргізілген. Барийдің арсениті мен арсенаты және антимоноит пен антимоноаттың тұрақтылық аймақтары анықталған.

Х.Б.Омаров, З.Б.Абсат, С.К.Алдабергенова, Н.Ж.Рахимжанова, А.Б.Каримова

Анализ свойств арсенатов и антимоноатов на основе диаграмм парциальных давлений

В статье по результатам термодинамических расчетов построены диаграммы парциальных давлений систем $Ba-O_2-SO_2-As_2$, $Ba-O_2-SO_2-Sb_2$. Проведен анализ взаимодействий соединений сурьмы и мышьяка в системах $Ba-O_2-SO_2-As_2$, $Ba-O_2-SO_2-Sb_2$ при 25 °С и 1 атм. общего давления. Определены области устойчивости арсената и арсенита бария, а также антимоноита и антимоноата бария.

References

- 1 Kasenov B.K., Aldabergenov M.K., Pashinkin A.S. *Thermodynamic methods in chemistry and metallurgy*, Almaty: Rauan, 1994, 126 p.

2 Pashinkin A.S., Spivak M.M., Malkova A.S. *Application diagrams partial pressures in metallurgy*, Moscow: Metallurgiya, 1984, 160 p.

3 *Chemist's Handbook*, Ed. B.P.Nikolsky, Leningrad: Nauka, 1971, 3, 1008 p.

4 Zhabekov M.I. *Abishev' readings – 2011: Heterogeneous processes in the enrichment and metallurgy*, Karaganda, 2011, p. 404–405.

Репозиторий Қарғу