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Concentration distribution of stibiumcontaining components and particles in oxycarboxylic acids solutions

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Abstract: In this work distribution of stibiumcontaining components and particles in the gas phase depending on the temperature (T =285-1005 K) in the following systems was researched: oxycarbonic acids - sulfides, stibium-oxide, stibium-water at different ratios of initial products. Formation of condensed substances of the following type was shown: Sb(c), Sb_2O_3(c), Sb_2SO_3(c), and also simple stibium compounds: Sb, Sb_2, Sb_3, Sb_4, SbO, Sb_4O_6, SbH, SbH_3 and SbS. The condensed stibium Sb (c) is formed within temperature alteration from 448 K up to 998K. It was noted that with increase of the temperature of conversion process the concentrations of: Sb, Sb_2, Sb_3, Sb_4, SbO, Sb_4O_6, SbH, SbH_3 and SbS increase, but concentrations of: Sb(c), Sb_2O_3(c), Sb_2SO_3(c) change in steps; maxima were noted at 648K. In the system $C_4H_6O_6$-Sb_2S_3-Sb_2O_3-H_2O three types of stibium oxides were found: SbO, Sb_2O_3(c), Sb_4O_6. In heterogeneous systems except stibiumcontaining substances also H,C,O,S -containing components and particles were formed. Formation of condensed stibium is connected with interaction of oxide and stibium sulfide with reducers of the following type: H_2, C(c), CO, CH_4.

Key words: *Stibium; Oxycarboxylic acid; Oxide; Sulfide; Concentration; Distribution*

1. Introduction

It is known that the main solvent for stibium compounds is mineral acids, sulfides and chlorides of alkaline metals, solutions of potassium (sodium) hydroxide, and among organic compounds in recent years in the technological purposes they often use oxycarboxylic acids, but their use as the main solvent by producing stibium and its compounds has purely analytical character (Usubakunov, M., 1981; Maimekov, Z., and others, 2013; Sambayeva, D., and others, 2013; Shabdanova, E., and others, 2013). Meanwhile, tartrate stibium solutions are steadier, they are not exposed to hydrolysis when heating and, especially at dilution with water. For example, increase of concentration of tartaric acid increases solubility of stibium trioxide.

It was noted that solubility of stibium trioxide has direct dependence on the dissociation constant of the used acids. Here it should be noted, that at dissolving stibium oxides and sulfides in solutions of organic oxyacids there is chemical balance between them that changes the speed of compound dissolution (Shabdanova, E., 2013). Respectively, studying physical and chemical characteristics of some heterogeneous systems (Shabdanova, E., 2014; Shabdanova, E., Tunguchbekova, Zh., and others, 2015): Sb_2O_3- Sb_2S_3-tartaric acid ($C_4H_6O_6$)-H_2O, Sb_2O_3- Sb_2S_3- citric acid ($C_6H_8O_7$)-H_2O, Sb_2O_3- Sb_2S_3 – malic acid ($C4H_6O_5$)-H_2O, Sb_2O_3-Sb_2S_3- succinic acid ($C_4H_6O_5$)-H_2O, Sb_2O_3- Sb_2S_3($C_4H_6O_5$)-H_2O, Sb_2O_3-Sb_2S_3- lactic acid ($C_3H_6O_3$)- H_2O, Sb_2O_3- Sb_2S_3 - glycolic acid ($C_2H_4O_3$) - H_2O with the purpose of establishing concentration distribution of stibiumcontaining components and particles in oxycarboxylic acids solutions at wide intervals of temperature alterations corresponding to the work mode of pyro -and hydrometallurgical leaching of stibium compounds is a topical scientific task.

2. Materials and the methods

The work considers the following heterogeneous systems: Sb_2O_3-Sb_2S_3-$C_4H_6O_6$-H_2O, Sb_2O_3-Sb_2S_3-$C_6H_8O_7$-H_2O, Sb_2O_3-Sb_2S_3-$C_4H_6O_5$-H_2O, Sb_2O_3-Sb_2S_3-$C_4H_6O_4$-H_2O, Sb_2O_3-Sb_2S_3-$C_3H_6O_3$-H_2O, Sb_2O_3-Sb_2S_3-$C_2H_4O_3$-H_2O for the purpose of establishing concentration distribution of stibiumcontaining components and particles at entropy maximum. The models that have a possibility of forming gaseous substances, electroneutral and ionized components formed the methodical basis of calculated parameters. The balanced data of components in the system are determined by solving the task about estimation of entropy extremum. The database of thermodynamic properties of individual substances includes information on Sb_2O_3, Sb_2S_3, H_2O, $C_4H_6O_6$,$C_6H_8O_7$, $C_4H_6O_5$, $C_4H_6O_4$, $C_3H_6O_3$, $C_2H_4O_3$

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(Sinyarev., G.,1982, Trusov, B., 1995, Maimekov, Z., 2015). Physical and chemical analysis of the gas phase was done on the basis of multifunctional gas analyzer Visit 01-L/LR. For measuring the content of solid particles the gas analyzer has a special built-in sounder. Along with gas concentration, the temperature of currents was also measured.

The main mode parameters of the gas analyzer changed over a wide range of temperature change. Concentration of components in the gas phase on the basis of measuring with gas analyzer of Visit 01 L/R is expressed in international units mln^{-1}. Recalculation of concentration values is done at corresponding values of temperature, pressure, molecular mass of some gases.

3. Results of the researches and their discussion

Distribution of stibium-containing components and particles in the gas phase (mol/kg) depending on the temperature (T =285-1005 K) in the following systems: $C_4H_6O_6$-Sb_2S_3- Sb_2O_3-H_2O, $C_6H_8O_7$ -Sb_2S_3-Sb_2O_3-H_2O, $C_2H_4O_3$- Sb_2S_3- Sb_2O_3-H_2O, $C_4H_6O_5$ -Sb_2S_3-Sb_2O_3-H_2O,$C_4H_6O_4$-Sb_2S_3-Sb_2O_3-H_2O, $C_3H_6O_3$ -Sb_2S_3-Sb_2O_3-H_2O,to P =0,1 MPa and ratios of initial products (3:1:1:1) at entropy maximum showed forming of condensed substances of the following type (tab. 1, fig. 1 and 2): Sb(c), Sb_2O_3(c), Sb_2SO_3(c), and also simple stibium compounds: Sb, Sb_2, Sb_3, Sb_4, SbO, Sb_4O_6, SbH, SbH_3 и SbS. Condensed Sb (c) stibium is formed within temperature alterations from 448 K up to 998K. Similar distribution of stibium-containing components and particles in the gas phase depending on temperature was noted also in some systems including tartaric acid, stibium oxide and water ($H_2C_4H_4O_6$-Sb_2O_3-H_2O (3:1:1), P =0.1 MPa, T=285-1005 K) and tartaric acid, stibium sulfide and water ($H_2C_4H_4O_6$-Sb_2S_3-H_2O (3:1:1), P =0.1 MPa, T=285-1005 K). From figures 1 and 2 we can see that with increase of temperature of conversion process the concentration of: Sb, Sb_2, Sb_3, Sb_4, SbO, Sb_4O_6, SbH, SbH_3 and SbS increase, but concentrations of: Sb(c), Sb_2O_3(c), Sb_2SO_3(c) change in steps; maxima were noted at the temperature 648K. In the system $C_4H_6O_6$-Sb_2S_3-Sb_2O_3-H_2O three types of stibium oxides were formed: SbO, Sb_2O_3(c), Sb_4O_6. In these heterogeneous systems except stibium-containing substances also: H,C,O,S -containing components and particles were formed: H, H_2, OH, H_2O, S, S_2, S_3, S_4, SO, SO_2, S_2O, SH, H_2S, SOH, H_2SO, C(c), CO, CO_2, CH_3, CH_4, C_2H_2, C_2H_4, C_2H_5, C_2H_6, C_3H_8, CHO, CHO_2, CH_2O, CH_2O_2, $C_2H_4O_2$, C_3H_6O, CS, CS_2, COS. Hence it follows that formation of condensed stibium is connected with interaction of stibium oxide and sulfide with reducers of the following type: H_2, C(c), CO, CH_4. The content of condensed carbon is from 7,443 mol/kg up to 0,374 mol/kg within temperature change from 298 K up to 748 K, and water from 18,361-9,418 mol/kg, molecular hydrogen 0,0001 - 8,371 mol/kg at temperature of 298-998K, respectively; carbon oxide CO = 0,0005-5,050 mol/kg at temperature of 498-998 K; carbon dioxide CO_2 = 5,439-10,226 mol/kg (298-748K), 10,226-8,223 mol/kg (798-998K); CH4 = 0,442-2,192 mol/kg (298-698K); C (c) of =7,443-0,374 mol/kg (298-748K); Sb(c) = 1,146-2,124 mol/kg (298-698K), 2,124-1,986 mol/kg (798-998K).

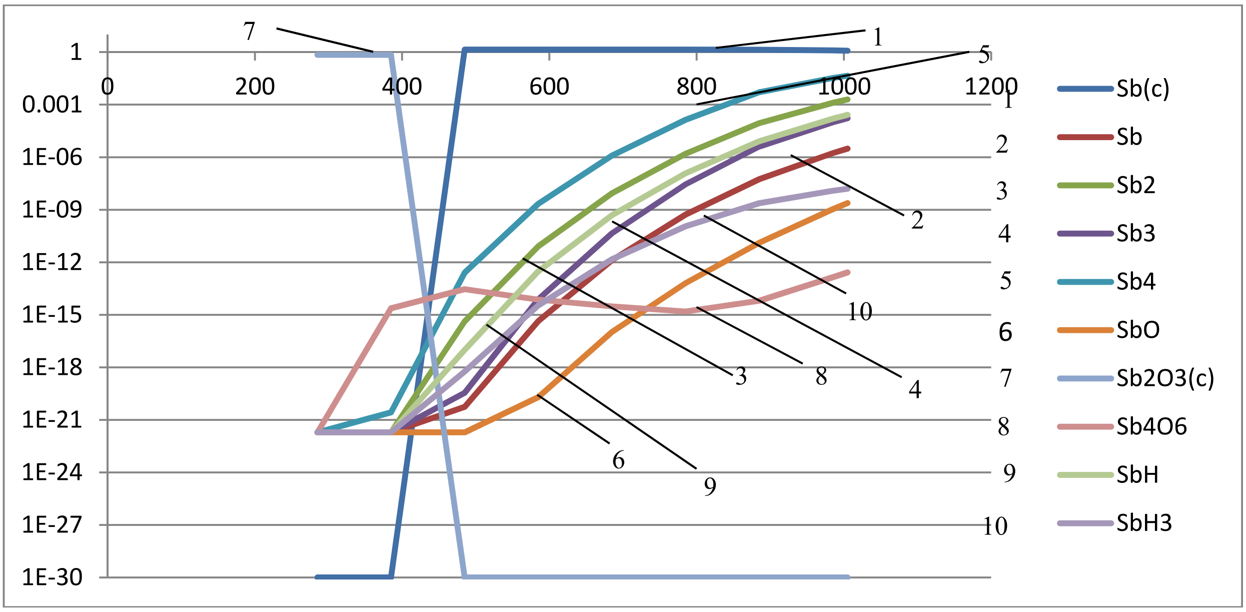

Fig. 1: Distribution of stibium-containing components and particles in the gas phase depending on the temperature in the system: $H_2C_4H_4O_6$-Sb_2O_3-H_2O (3:1:1) at P =0.1 MPa, T=285-1005 K

Table 1: Distribution of stibium-containing components and particles in the gas phase (mol/kg) depending on the temperature in the systems at P =0,1 MPa and ratios of initial products (3:1:1:1)

(**With tartaric acid $C_4H_6O_6$-Sb_2S_3- Sb_2O_3-H_2O**)

T	Sb(c)	Sb	Sb_2	Sb_3	Sb_4	SbO
448	1,14691	1,93E-22	2,92E-18	1,93E-22	2,58E-15	1,93E-22
548	1,23761	9,11E-18	2,69E-13	1,15E-16	9,35E-11	3,1E-22
598	1,45764	1,21E-15	1,93E-11	2,35E-14	4,66E-09	5,92E-20
648	1,97871	7,68E-14	7,18E-10	2,11E-12	1,26E-07	5,08E-18
698	2,12483	2,68E-12	1,57E-08	9,78E-11	2,1E-06	2,28E-16
998	1,98692	2,1E-06	0,001412	0,000116	0,033582	1,67E-09
T	**Sb_2O_3(c)**	**Sb_4O_6**	**SbH**	**SbH_3**	**SbS**	**Sb_2S_3(c)**
448	2,86E-30	4,73E-14	5,59E-20	7,05E-21	4,79E-18	0,488961
548	2,86E-30	9,58E-15	8,49E-15	1,67E-16	4,29E-13	0,443613
598	2,86E-30	5,5E-15	7,53E-13	6,92E-15	3,26E-11	0,333596
648	2,86E-30	3,53E-15	3,36E-11	1,51E-13	1,28E-09	0,073061
698	2,86E-30	2,37E-15	8,81E-10	2,11E-12	1,5E-08	2,86E-30
998	2,86E-30	3,16E-13	0,000172	9,94E-09	0,000243	2,86E-30
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With citric acid $C_6H_8O_7$ -Sb_2S_3- Sb_2O_3-H_2O

T	Sb(c)	Sb	Sb_2	Sb_3	Sb_4	SbO
448	1,14707	1,93E-22	2,84E-18	1,93E-22	2,51E-15	1,93E-22
548	1,24087	8,87E-18	2,62E-13	1,12E-16	9,1E-11	2,9E-22
598	1,46744	1,18E-15	1,88E-11	2,29E-14	4,54E-09	5,56E-20
648	2,00307	7,49E-14	7,01E-10	2,06E-12	1,23E-07	4,79E-18
698	2,12483	2,61E-12	1,54E-08	9,55E-11	2,05E-06	2,16E-16
998	1,97594	2,27E-06	0,001525	0,000126	0,036266	9,18E-10
T	**Sb_2O_3(c**	**Sb_4O_6**	**SbH**	**SbH_3**	**SbS**	**Sb_2S_3(c)**
448	2,86E-30	3,53E-15	5,64E-20	7,66E-21	3,87E-18	0,488881
548	2,86E-30	3,98E-18	8,52E-15	1,78E-16	4,17E-13	0,441983
598	2,86E-30	2,23E-12	7,55E-13	7,34E-15	3,18E-11	0,328694
648	1E-30	4,17E-13	3,37E-11	1,6E-13	1,24E-09	0,060882
698	2,86E-30	2,61E-12	8,84E-10	2,23E-12	1,42E-08	2,86E-30
998	2,86E-30	4,54E-09	0,00021	1,54E-08	0,000189	2,86E-30
Z.Maimekov, E.Shabdanova, 2013						

With glycolic acid $C_2H_4O_3$- Sb_2S_3- Sb_2O_3-H_2O

T	Sb(c)	Sb	Sb_2	Sb_3	Sb_4
448	1,14767	1,93E-22	3,09E-18	1,93E-22	2,73E-15
548	1,25584	9,65E-18	2,85E-13	1,21E-16	9,9E-11
598	1,51605	1,29E-15	2,05E-11	2,49E-14	4,94E-09
648	2,12483	8,17E-14	7,64E-10	2,24E-12	1,34E-07
898	2,09671	8,56E-08	0,000125	6,47E-06	0,006957
998	1,97443	2,29E-06	0,00154	0,000127	0,036632
T	**Sb_2O_3(c)**	**SbH**	**SbH_3**	**SbS**	**Sb_2S_3(c)**
448	2,86E-30	6,36E-20	9,27E-21	4,21E-18	0,488582
548	2,86E-30	9,54E-15	2,12E-16	4,54E-13	0,434495
598	2,86E-30	9,54E-15	2,12E-16	4,54E-13	0,434495
648	2,86E-30	3,77E-11	1,88E-13	1,35E-09	2,38E-18
898	2,86E-30	0,000012	2,98E-09	1,54E-05	2,86E-30

998	1,5E-09	2,86E-30	0,000205	1,41E-08	0,000205

With malic acid $C_4H_6O_5$ -Sb_2S_3- Sb_2O_3-H_2O

T	Sb(c)	Sb	Sb_2	Sb_3	Sb_4	SbO
448	0,766494	1,93E-22	3,04E-18	1,93E-22	2,69E-15	1,93E-22
548	0,874337	9,51E-18	2,81E-13	1,2E-16	9,76E-11	2,96E-22
598	1,13353	1,27E-15	2,02E-11	2,45E-14	4,87E-09	5,7E-20
648	1,74505	8,06E-14	7,53E-10	2,21E-12	1,33E-07	4,93E-18
698	2,07076	2,83E-12	1,66E-08	1,03E-10	2,21E-06	2,24E-16
998	1,92037	2,29E-06	0,001539	0,000127	0,036615	1,41E-09
T	**Sb_2O_3(c)**	**SbH**	**SbH_3**	**SbS**	**Sb_2S_3(c)**	
448	2,86E-30	6,31E-20	9,33E-21	4,15E-18	0,652136	
548	2,86E-30	9,46E-15	2,13E-16	4,47E-13	0,598214	
598	2,86E-30	8,37E-13	8,69E-15	3,41E-11	0,468617	
648	2,86E-30	3,73E-11	1,88E-13	1,34E-09	0,162858	
698	2,86E-30	9,77E-10	2,58E-12	1,81E-08	2,86E-30	
998	2,86E-30	0,000205	1,4E-08	0,000273	2,86E-30	

With succinic acid $C_4H_6O_4$ -Sb_2S_3- Sb_2O_3-H_2O

T	Sb(c)	Sb	Sb_2	Sb_3	Sb_4	SbO
448	1,14768	1,93E-22	2,9E-18	1,93E-22	2,56E-15	1,93E-22
548	1,25491	9,07E-18	2,68E-13	1,14E-16	9,3E-11	2,73E-22
598	1,51183	1,21E-15	1,93E-11	2,34E-14	4,65E-09	5,27E-20
648	2,11729	7,7E-14	7,19E-10	2,11E-12	1,27E-07	4,57E-18
698	2,12483	2,68E-12	1,58E-08	9,79E-11	2,1E-06	2,07E-16
998	1,96164	2,48E-06	0,001672	0,000138	0,039757	6,38E-10
T	**Sb_2O_3(c)**	**SbH**	**SbH_3**	**SbS**	**Sb_2S_3(c)**	
448	2,86E-30	6,18E-20	9,62E-21	3,95E-18	0,488575	
548	2,86E-30	9,21E-15	2,16E-16	4,26E-13	0,43496	
598	2,86E-30	8,14E-13	8,8E-15	3,25E-11	0,3065	
648	1E-30	3,63E-11	1,9E-13	1,28E-09	0,003769	
698	2,86E-30	9,55E-10	2,67E-12	1,28E-08	2,86E-30	
998	2,86E-30	0,000249	2,15E-08	0,000162	2,86E-30	

With lactic acid $C_3H_6O_3$ -Sb_2S_3- Sb_2O_3-H_2O

T	Sb(c)	Sb	Sb_2	Sb_3	Sb_4	SbO
448	1,14871	1,93E-22	3,11E-18	1,93E-22	2,75E-15	1,93E-22
548	1,27856	9,75E-18	2,88E-13	1,23E-16	1E-10	2,65E-22
598	1,58697	1,3E-15	2,08E-11	2,52E-14	5E-09	5,16E-20
648	2,12483	8,28E-14	7,74E-10	2,27E-12	1,36E-07	4,5E-18
948	2,0426	5,67E-07	0,000557	3,72E-05	0,020223	8,76E-11
998	1,94673	2,71E-06	0,001824	0,00015	0,043393	6,3E-10
T	**Sb_2O_3(c)**	**SbH**	**SbH_3**	**SbS**	**Sb_2O_3(c)**	
448	2,86E-30	7,14E-20	1,29E-20	4,25E-18	0,488062	
548	2,86E-30	1,05E-14	2,78E-16	4,58E-13	0,423137	
598	2,86E-30	9,27E-13	1,12E-14	3,5E-11	0,268931	
648	2,86E-30	4,14E-11	2,44E-13	1,15E-09	4,5E-23	
948	2,86E-30	7,26E-05	1,24E-08	4,47E-05	2,86E-30	
998	2,86E-30	0,000287	2,77E-08	0,000145	2,86E-30	

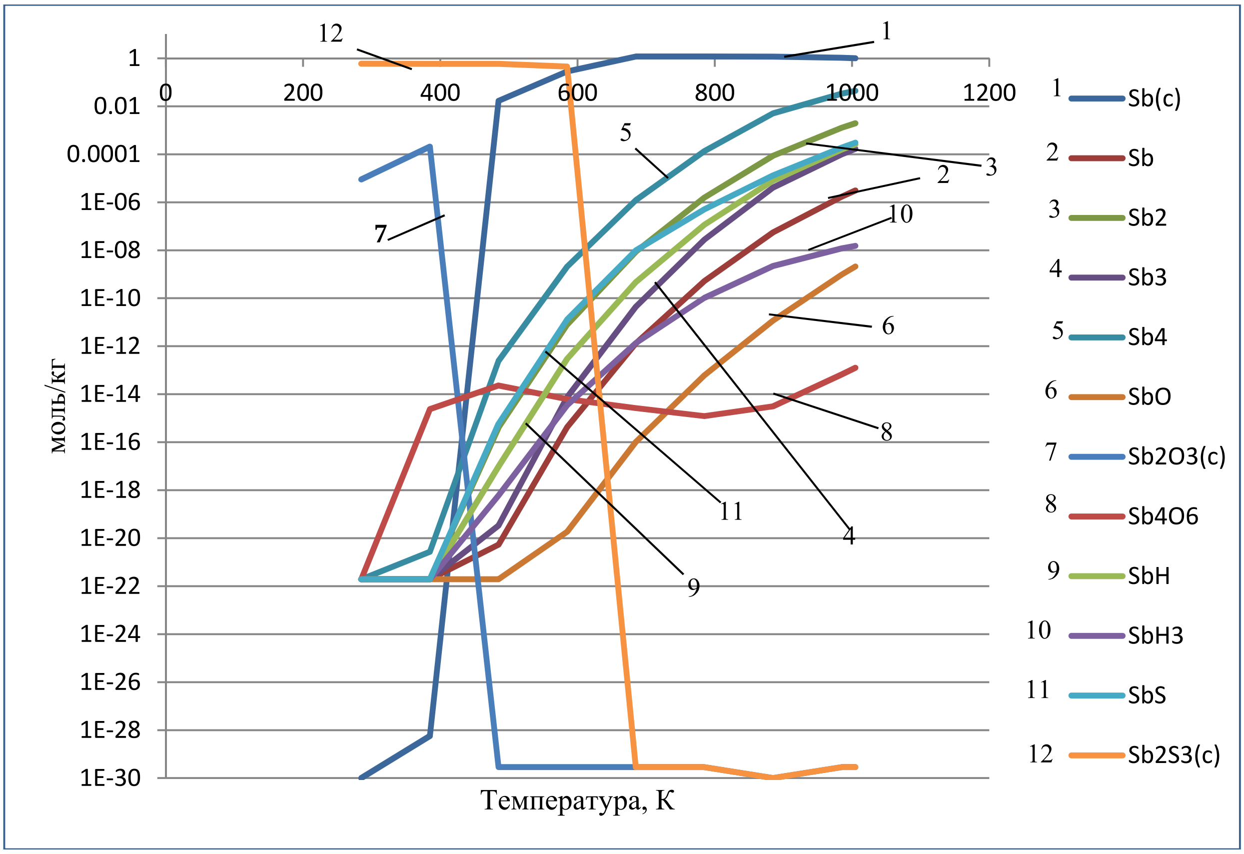

Fig. 2: Distribution of stibium-containing components and particles in the gas phase depending on the temperature in the system: $H_2C_4H_4O_6$-Sb_2S_3-H_2O (3:1:1) at P =0.1 MPas, T=285-1005

Thus, concentration distribution of stibium containing components and particles in oxycarboxylic acids solutions (fig. 1 and 2, tab. 1) showed formation of different stibium containing components and particles of the following type: Sb, Sb_2, Sb_3, Sb_4, SbO, Sb_4O_6, SbH, SbH_3, SbS, Sb(c), Sb_2O_3(c), Sb_2SO_3(c). At the same time the content of condensed stibium in the temperature limits 448-998K is 1.1487-1.9467 mol/kg, and condensed stibium sulfide is from 0,65 to 0,16 in the temperature limits from 448-648K, at the same time the amount of stibium trioxide in the gas phase is minimum and equals to 2,86E - 30 mol/kg. Correspondingly, the optimum mode of receiving stibium in pyrometallurgical processes varies within 448-998K.

4. Conclusions

1. The following systems were studied: stibium oxide (sulfide) - oxycarboxylic acids- H_2O at wide intervals of temperature change corresponding to the operating mode of pyrometallurgical processes of stibium sublimation from its sparingly soluble compounds.

2. Equilibrium compositions and concentration of components in the following systems were determined: oxide, stibium-sulfide, stibium – oxycarboxylic acides- H_2O and concentration distribution of Sb, C, H, O, S-containing components and particles in the gas phase at wide intervals of temperature change and ratios of initial components was also established. The obtained data enable to determine the limiting stages of the stibium sublimation process enabling to predict efficiency of doing mining works.

3. Equilibrium compositions and concentration of decomposition products of stibium oxide and sulfide with oxycarboxylic acids showed that in the gas phase stibium compounds turn into the form of the following type: Sb(c), Sb, Sb_2 , Sb_3, Sb_4, SbO, Sb_2O_3(c), Sb_4O_6, SbH, SbH_3, SbS, Sb_2S_3(c). Condensed stibium Sb (c) is formed within temperature change from 448 K to 998K.

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