



Physical CHEMISTRY

An Indian Journal

Full Paper

PCAIJ, 10(3), 2015 [090-095]

The Gibbs energy increments for minerals of Pb-jarosite group

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ABSTRACT

The linear decomposition of standard Gibbs potentials ($\Delta_f G^\circ$) values on chemical elements for three synthetic Pb-As, Pb-Cu, and Pb-Zn jarosites^[6] have been calculated by means of linear programming problems. Comparison the errors of calculations $\Delta_f G^\circ$ with published data does not exceed on the average 1 %. The received equations have been used in calculations of Gibbs potentials for minerals with unknown thermodynamic properties. © 2015 Trade Science Inc. - INDIA

KEYWORDS

The standard Gibbs potentials of formation from the elements;
Pb-jarosites;
Hyroxosulphates and hydroxoarsenates;
Linear programming.

INTRODUCTION

Minerals of the jarosite group can be represented by the general formula:



where A are a cations with a coordination number ≥ 9 , often presented by K^+ , Na^+ , H_3O^+ , NH_4^+ ; B and T - cations of octahedral and tetrahedral coordination respectively. The B cations are more presented by Fe^{3+} ions, and anions TO_4 by sulfates, the ideal formula of jarosite - $KFe_3(SO_4)_2(OH)_6$. At positions A and B in the formula (1) may be the divalent metal cations - Pb^{2+} , Cu^{2+} , Zn^{2+} , and the positions of the T - cations As^{5+} , Se^{6+} . It is known the inclusion in the structure of jarosite three and hexavalent chromium with the formation of compounds $KCr_3(SO_4)_2(OH)_6$ and $KFe_3(CrO_4)_2(OH)_6$, respectively^[3], and such elements as Cd, Ga, Hg and others^[5,6].

Minerals of the jarosite group are often formed

in the zone of hypergenesis, the oxidation zones of sulfide deposits, the mining and metallurgical landscapes^[17]. Probably is the widespread presence of jarosites in the conditions of the Martian surface^[16]. Interest in Pb-jarosites is caused by their low solubility in aqueous solutions in comparison with other minerals of this group. For this reason the Pb-jarosites have been exploited as purifiers on technological solutions in the metallurgical industries^[4] and they may be accumulators of toxic elements in environment, for example arsenic in the form of minerals beudantite - $PbFe_3(AsO_4)_2(SO_4)_2(OH)_6$, hidalgoite $PbAl_3(AsO_4)_2(SO_4)_2(OH)_6$ and others^[9-12]. Thermodynamic characteristics of Pb-containing jarosites make possible to estimate the directions of the dissolution and precipitation processes in aqueous solutions. The aim of this work is to obtain the linear decomposition on chemical elements for the values of standard Gibbs energies for mineral of the Pb-jarosite group and estimate the potentials of these classes minerals

TABLE 1 : The values of standard Gibbs energies of formation from the elements - $\Delta_f G^\circ$ (J/mol) for components of reactions (2-4)

Component	$-\Delta_f G^\circ$ (J/mol)
PbO	188950
Fe ₂ O ₃	742099
SO ₃	371170
As ₂ O ₅	782400
H ₂ O	237181
O ₂	0
CuO	129500
ZnO	320700
(H ₃ O) _{0.68} Pb _{0.32} Fe _{2.86} (SO ₄) _{1.69} (AsO ₄) _{0.31} (OH) _{5.59} (H ₂ O) _{0.41}	3164800
(H ₃ O) _{0.67} Pb _{0.33} Fe _{2.71} Cu _{0.25} (SO ₄) ₂ (OH) _{5.96} (H ₂ O) _{0.04}	3131400
(H ₃ O) _{0.57} Pb _{0.43} Fe _{2.7} Zn _{0.21} (SO ₄) ₂ (OH) _{5.95} (H ₂ O) _{0.05}	3153600

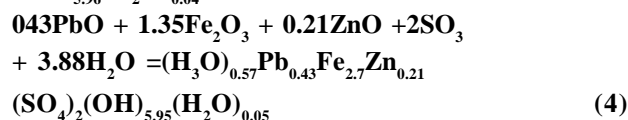
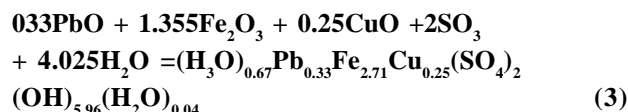
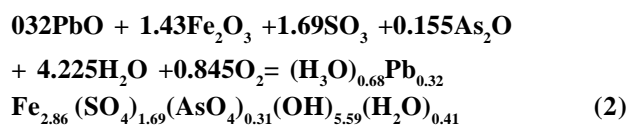
TABLE 2 : The values of standard Gibbs energies of formation from the elements - $\Delta_f G^\circ$ (J/mol) for minerals of the jarosite group, calculated with equations (5-7) in comparison with the literature data. Relative errors of the estimates are given in percent

Mineral	Literature data	Calculation by equations		
		(5)	(6)	(7)
(H ₃ O) _{0.68} Pb _{0.32} Fe _{2.86} (SO ₄) _{1.69} (AsO ₄) _{0.31} (OH) _{5.59} (H ₂ O) _{0.41} (Pb-As-jarosite)	3164800 ^[6]	3164800 (0.00)		
(H ₃ O) _{0.67} Pb _{0.33} Fe _{2.71} Cu _{0.25} (SO ₄) ₂ (OH) _{5.96} (H ₂ O) _{0.04} (Pb-Cu-jarosite)	3131400 ^[6]	3096837 (1.11)	3131400 (0.00)	3156450 (0.80)
(H ₃ O) _{0.57} Pb _{0.43} Fe _{2.7} Zn _{0.21} (SO ₄) ₂ (OH) _{5.95} (H ₂ O) _{0.05} (Pb-Zn-jarosite)	3153600 ^[6]	3074163 (2.55)	3104873 (1.56)	3153600 (0.00)
Fe ₅ (SO ₄) ₆ (OH) ₂ ·20H ₂ O (copiapite)	9971000 ^[1]	9892316 (0.79)	9982140 (0.11)	10016444 (0.45)
(H ₃ O)Fe ₃ (SO ₄) ₂ (OH) ₆ (hydroxonium-jarosite)	3232500 ^[1]	3205900 (0.83)	3235212 (0.08)	3245830 (0.41)
Fe ₅ (SO ₄) ₆ O(OH)·20H ₂ O (ferricopiapite)	9899000 ^[1]	9849748 (0.50)	9948425 (0.50)	9984998 (0.86)
Fe _{4.78} (SO ₄) ₆ (OH) _{2.34} ·20.71H ₂ O (ferricopiapite)	10089800 ^[1]	10119926 (0.30)	10222316 (1.30)	10259445 (1.67)
PbFe ₃ (AsO ₄)(SO ₄)(OH) ₆ (beudantite)	3055600 ^[2]	3084719 (0.95)		
Fe ₂ (AsO ₄)(SO ₄)(OH)·7H ₂ O (bukovskiite)	3480000 ^[2]	3596905 (3.30)		
Mean relative error, δ (%)		0.81	0.59	0.70

with unknown properties.

METHODS

The synthetic Pb-As, Pb-Cu and Pb-Zn jarosite have been chosen as calibration substances^[6]. For the reactions of their formation from oxides:



by means of linear programming problems^[18-22] the molar increments of the Gibbs energies $\Delta_f G^\circ$ (kJ/mol) have been obtained in the form of corresponding linear dependencies:

$$\Delta_f G^\circ = -3164.800 = -83.701y_{\text{Pb}} - 134.369y_{\text{Fe}}$$

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TABLE 3 : The values of standard Gibbs energies of formation from the elements $-\Delta_f G^\circ$ (J/mol) for minerals of chemical classes -hydroxosulfates and hydroxoarsenates of iron, lead, copper and zinc

Mineral	Calculation by equations		
	(5)	(6)	(7)
Fe(SO ₄)(OH)·5H ₂ O (fibroferrite)	2212508	2269839	2276448
Fe(SO ₄)(OH)·2H ₂ O (butlerite)	1471592	1484301	1490013
Pb _{0.5} Fe ₃ (SO ₄) ₂ (OH) ₆ (plumbojarosite)	2969410	2970861	2978110
PbFe ₃ (SO ₄) ₂ (OH) ₆ (beaverite)	3037920	3002069	3003981
Pb _{0.94} Fe _{1.74} Cu _{1.12} (SO ₄) ₂ (OH) ₆ (beaverite-Cu)	2764581	2876034	2887357
PbCuFe ₂ (SO ₄) ₂ (OH) ₆ (osarizawaite)	2828616	2906120	2915941
CuFe ₂ (SO ₄) ₂ (OH)·2H ₂ O (guildite)	2277614	2226738	2234996
PbFe ₂ Zn(SO ₄) ₂ (OH) ₆ (beaverite-Zn)	3007189	3084694	3094515
FeZn(SO ₄) ₂ (OH)·7H ₂ O (zinkobotryogen) ^[23]	3471785	3608633	3626297
Fe ₆ (AsO ₄) ₄ (SO ₄)(OH) ₄ ·H ₂ O (tooeleite) ^[15]	4856979		
Fe ₂ (AsO ₄)(SO ₄)(OH)·5H ₂ O (sarmientite) ^[10]	3045790		
Fe ₄ (AsO ₄) ₃ (SO ₄)(OH)·15H ₂ O (zykaite) ^[12]	7182075		
PbFe ₂ (AsO ₄) ₂ (OH) ₂ (carminite) ^[23]	2166756		
Cu ₂ Fe ₂ (AsO ₄) ₂ (OH) ₄ ·H ₂ O (chenevixite) ^[8]	2659794		
Cu ₁₀ (SO ₄)(AsO ₄) ₄ (OH) ₆ ·8H ₂ O (leogangite) ^[14]	6197750		
CuFe ₂ (AsO ₄) ₂ (OH) ₂ ·4H ₂ O (arthurite) ^[23]	3027581		
Cu ₉ (SO ₄)(AsO ₄) ₂ (OH) ₁₀ ·7H ₂ O (parnaute) ^[7]	5439120		
Cu ₈ (AsO ₄) ₄ (OH) ₄ ·5H ₂ O (strashimirite) ^[13]	4496947		

$+91.961y_s - 4.433y_{As} - 173.574y_o - 42.568y_H$ (5) in (TABLE 2).

$\Delta_f G^\circ = -3131.400 = -62.417y_{Pb} - 105.908y_{Fe}$
 $-9.959y_{Cu} + 151.098y_s - 194.417y_o - 33.715y_H$ (6)

$\Delta_f G^\circ = -3153.600 = -51.741y_{Pb} - 98.000y_{Fe}$
 $-188.533y_{Zn} + 159.998y_s - 199.255y_o - 31.446y_H$ (7)

where y_i is the stoichiometric coefficients of the chemical elements i in the formula (1).

The used values of Gibbs potentials for components of reactions (2-4) are presented in (TABLE 1). The relative error of calculations by equations (5-7) with published data for minerals of iron and lead hydroxosulfates and hydroxoarsenates are shown

RESULTS AND DISCUSSIONS

Comparing equations (5-7) as bar diagrams (Figure 1-3) it can be seen that the decomposition (5-7) are similar. The decomposition (5) can be used for estimations of iron and lead hydroxosulfates and hydroxoarsenates. Moreover the calculations with the usage of equation (5) can be applied for Cu and Zn containing compounds with involving the values of copper and zinc increments from the expressions (6) and (7). With this in mind we calculated the val-

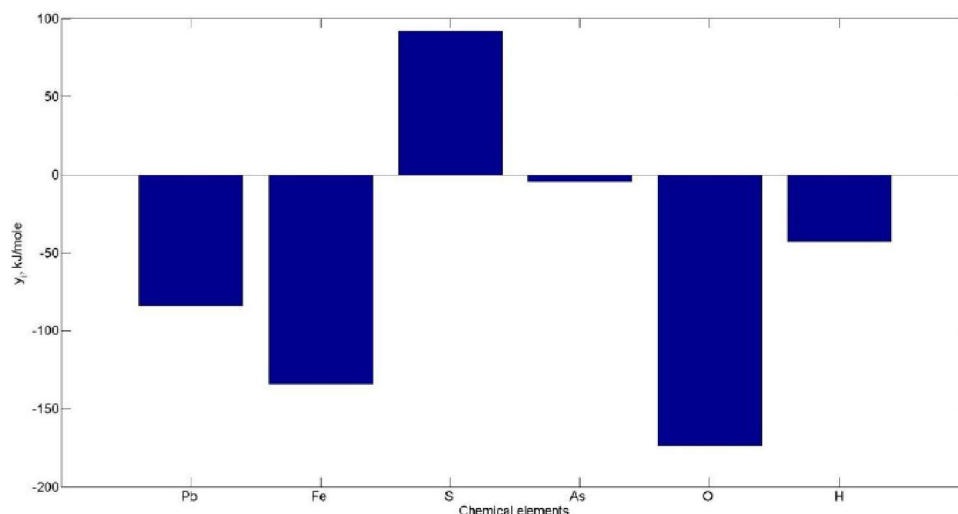


Figure 1 : The linear decomposition of value Gibbs free energy $\Delta_f G^\circ = -3164800$ (J/mole) for Pb-As-jarosite $(H_3O)_{0.68}Pb_{0.32}Fe_{2.86}(SO_4)_{1.69}(AsO_4)_{0.31}(OH)_{5.59}(H_2O)_{0.41}$ on chemical elements increments

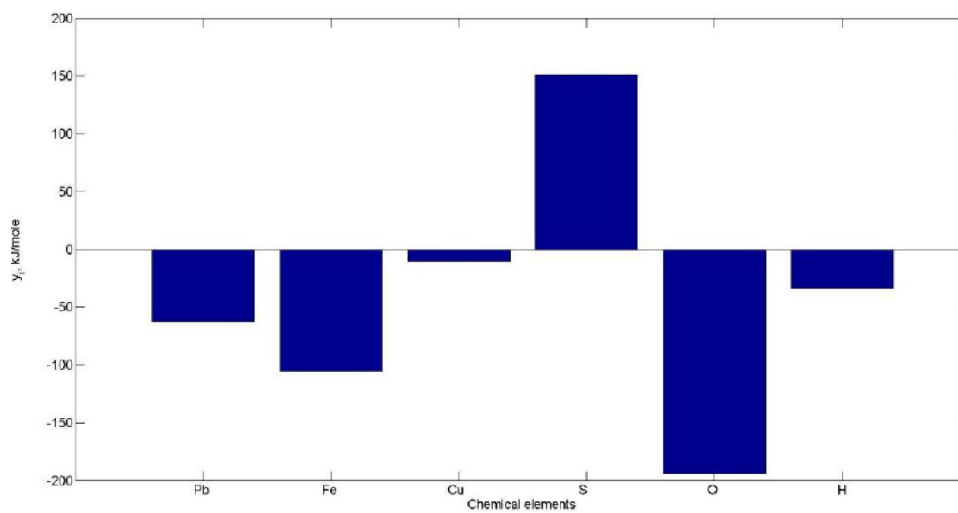


Figure 2 : The linear decomposition of value Gibbs free energy $\Delta_f G^\circ = -3131400$ (J/mole) for Pb-Cu-jarosite $(H_3O)_{0.67}Pb_{0.33}Fe_{2.71}Cu_{0.25}(SO_4)_2(OH)_{5.96}(H_2O)_{0.04}$ on chemical elements increments

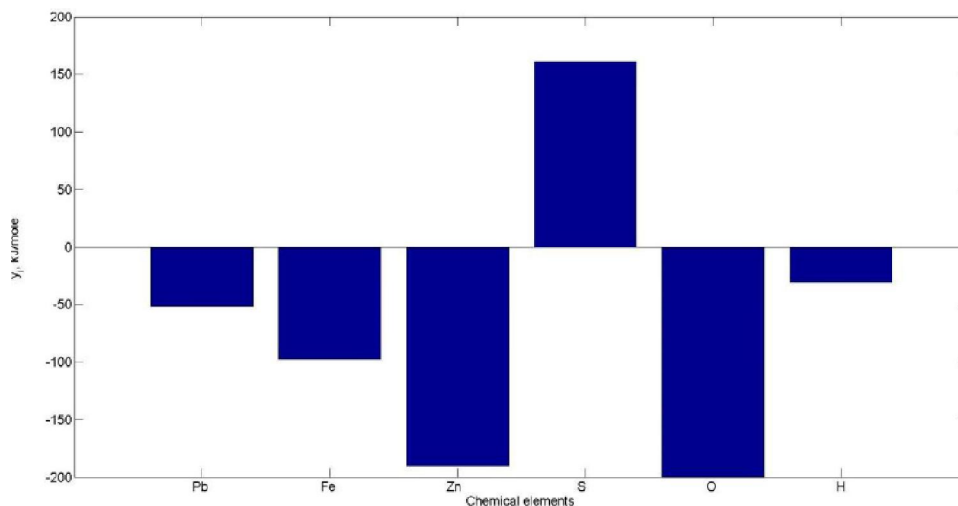


Figure 3 : The linear decomposition of value Gibbs free energy $\Delta_f G^\circ = -3153600$ (J/mole) for Pb-Zn-jarosite $(H_3O)_{0.57}Pb_{0.43}Fe_{2.7}Zn_{0.21}(SO_4)_2(OH)_{5.95}(H_2O)_{0.05}$ on chemical elements increments

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ues of the Gibbs energies of some minerals with unknown properties (TABLE 3). The equations (5-7) can be used for estimations the standard Gibbs potentials for complex minerals of hydroxosulfates and hydroxoarsenates classes of iron, lead, copper, and zinc.

REFERENCES

- [1] M.V.Charykova, V.G.Krivovichev, w.Depmeir; Thermodynamics of arsenates, selenites, and sulfates of the oxidation zone of sulphide ores: I. Thermodynamic constants at ambient conditions// *Geology of Ore Deposits*, **52**, 8, 689-700 (2010).
- [2] P.Drahota, M.Filippi; Secondary arsenic minerals in the environment: A review// *Environment International*, **35**, 1243-1255 (2009).
- [3] C.Drouet, D.Baron, A.Navrotsky; On the thermochemistry of the solid solution between jarosite and its chromate analog// *Am.Mineral*, **88**, 1949–1954 (2003).
- [4] J.E.Dutrizac, J.Jambor; Jarosites and their application in hydrometallurgy in: P.H. Ribbe (Ed.), *Reviews in Mineralogy and Geochemistry: Sulfate Minerals*, Mineralogical Society of America, Washington, DC, **40**, 405–443 (2000).
- [5] F.L.Forray, A.M.L.Smith, C.Drouet, A.Navrotsky, K.Wright, Hudson K.A.Edwards, W.E.Dubbin; Synthesis, Characterization and thermochemistry of a Pb-jarosite// *Geochimica et Cosmochimica Acta*, **74**, 215-224 (2010).
- [6] F.L.Forray, A.M.L.Smith, A.Navrotsky, K.Wright, Hudson K.A.Edwards, W.E.Dubbin; Synthesis, Characterization and thermochemistry of synthetic Pb-As, Pb-Cu and Pb-Zn jarosites// *Geochimica et Cosmochimica Acta*, **127**, 107-119 (2014).
- [7] R.L.Frost, E.C.Keeffe; The mixed anion mineral parnaute $\text{Cu}_9[(\text{OH})_{10}[\text{SO}_4](\text{AsO}_4)_2] \cdot 7\text{H}_2\text{O}$ —A Raman spectroscopic study// *Spectrochimica Acta Part A*, **81**, 111–116 (2011).
- [8] R.L.Frost, A.Lopez, R.Scholz, C.Lana, Y.Xi; A Raman spectroscopic study of the arsenate mineral chenevixite $\text{Cu}_2\text{Fe}_2(\text{AsO}_4)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$ // *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **135**, 192–197 (2015).
- [9] R.L.Frost, S.J.Palmer, H.J.Spratt, W.N.Martens; The molecular structure of the mineral beudantite $\text{PbFe}_3(\text{AsO}_4, \text{SO}_4)_2(\text{OH})_6$ —Implications for arsenic accumulation and removal// *Journal of Molecular Structure*, **988**, 52–58 (2011).
- [10] R.L.Frost, S.J.Palmer, Y.Xi; The molecular structure of the mineral sarmientite $\text{Fe}_2(\text{AsO}_4, \text{SO}_4)_2(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ —Implications for arsenic accumulation and removal// *Journal of Molecular Structure*, **1004**, 88–93 (2011).
- [11] R.L.Frost, S.J.Palmer, Y.Xi; The molecular structure of the multianion mineral hidalgoite $\text{PbAl}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$ —Implications for arsenic removal from soils// *Journal of Molecular Structure*, **1005**, 214–219 (2011).
- [12] R.L.Frost, S.J.Palmer, Y.Xi; Vibrational spectroscopy of the multi-anion mineral zykaite $\text{Fe}_4(\text{AsO}_4)(\text{SO}_4)(\text{OH}) \cdot 15\text{H}_2\text{O}$ —implications for arsenate removal// *Spectrochimica Acta Part A*, **83**, 444–448 (2011).
- [13] R.L.Frost, J.Sejkora, J.Cejka, E.C.Keeffe; Vibrational spectroscopic study of the arsenate mineral strashimirite $\text{Cu}_8(\text{AsO}_4)_4(\text{OH})_4 \cdot 5\text{H}_2\text{O}$ —Relationship to other basic copper arsenates// *Vibrational Spectroscopy*, **50**, 289–297 (2009).
- [14] R.L.Frost, Y.Xi, S.J.Palmer; The structure of the mineral leogangite $\text{Cu}_{10}(\text{OH})_6(\text{SO}_4)(\text{AsO}_4)_4 \cdot 8\text{H}_2\text{O}$ —Implications for arsenic accumulation and removal// *Spectrochimica Acta Part A*, **82**, 221–227 (2011).
- [15] J.Liu, S.Deng, F.Zhao, H.Cheng, R.L.Frost; Spectroscopic characterization and solubility investigation on the effects of As(V) on mineral structure tooeleite $(\text{Fe}_6(\text{AsO}_3)_4\text{SO}_4(\text{OH})_4 \cdot \text{H}_2\text{O})$ // *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **134**, 428–433 (2015).
- [16] A.Navrotsky, F.L.Forray, C.Drouet; Jarosite stability on Mars// *Icarus*, **176**, 250–253 (2005).
- [17] R.E.Stoffregen, C.N.Alpers, J.L.Jambor; Alunite-jarosite crystallography, thermodynamics, and geochemistry, in: P.H.Ribbe (Ed.), *Reviews in Mineralogy and Geochemistry: Sulfate Minerals*, Mineralogical Society of America, Washington, DC, **40**, 454–479 (2000).
- [18] O.V.Yeromin; Evaluation of standard thermodynamic potentials for natural zeolites in unified stoichiometric formulas// *Journal of Earth Science Research*, **1**, 3, 84-93 (2013).
- [19] O.V.Yeromin; Calculation of standard thermodynamic potentials for Na-zeolites with the use of linear programming problems. *International Journal of Geosciences*, **3**, 227-230 (2011).
- [20] O.V.Yeromin, G.A.Yurgenson; Calculation of standard thermodynamic potentials of natural calcium

- zeolites//Zeitschrift für Geologische Wissenschaften, **4**, 245-251 (2012).
- [21] O.V.Eremin; Estimation of the standard thermodynamic potentials of framework Ca-aluminosilicates by linear programming//Geochimiya, [In Russian], **9**, 859-864 (2014).
- [22] O.V.Eremin, S.V.Vinnichenko, G.A.Yurgenson; Calculation of standard Gibbs potentials for copper hydroxosulfates with crystal water by means of dual linear programming problems//Doklady Akademii Nauk, [In Russian], **409(3)**, 386-388 (2006).
- [23] [http://mincryst.iem.ac.ru/Crystallographic and Crystallochemical Database for Minerals and their Structural Analogues](http://mincryst.iem.ac.ru/Crystallographic%20and%20Crystallochemical%20Database%20for%20Minerals%20and%20their%20Structural%20Analogues)