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AN EMPIRICAL APPROACH TO THE ESTIMATION OF STANDARD ENTROPIES OF BINARY, TERNARY AND HIGHER COMPONENT SULFIDES

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Проанализирована гипотеза о взаимосвязи различий в значениях стандартной энтропии, наблюдаемых в рядах химических аналогов, и приведенных масс этих соединений. Получен ряд корреляционных уравнений, отражающих зависимости приведенных масс химических связей в соединениях и позволяющих определить стандартную энтропию бинарных сульфидов. Определены закономерности взаимосвязи подходящих к корреляционным уравнениям констант для разных групп сходных соединений. На основе найденных корреляций предложены простые схемы довольно точного прогнозирования. Принцип аддитивности энтропии успешно применен для прогнозирования энтропии трех-, четырех- и более компонентных сульфидов. Средние отклонения значений стандартной энтропии, определяемых с помощью выявленных корреляций, от экспериментально найденных или справочных данных находятся в пределах $\pm(1-5)$ %.

The idea that the reduced masses difference accounts for almost all of the differences in entropy among chemically similar compounds is exploited. A range of correlation equations that rely on the reduced mass of the chemical bonds in a compound to estimate the standard entropy of binary sulfides have been obtained. The regularities that link together fitting constants of correlation equations for different groups of similar compounds have been revealed. Based on the obtained correlations, simple and well defined predictive schemes are proposed. The additivity principle for entropy has been successfully applied for the entropy prediction of ternary, quaternary and higher component sulfides. The mean deviations of the standard entropy estimations from experimental and/or tabulated data using the obtained correlations are in the range of $\pm(1-5)$ %.

Ключевые слова: стандартная энтропия; трех-, четырех- и более компонентные сульфиды; корреляционные уравнения; константы.

Keywords: standard entropy; ternary, quaternary and higher component sulfides; correlation equations; fitting constants.

Sulfides, as binary and ternary, and higher component phases such as Chevrel phases, are of a interest due to their current and potential applications, such as photovoltaics [1, 2], battery electrodes [3–5], thermoelectric materials [6]. Thermodynamic calculations provide a powerful tool for prediction of chemical behavior of the materials in different environments, their thermal stability during thermal processing and the phase stability. Phase diagrams are widely used in the material science. However, their experimental determination is very time consuming. Computational thermodynamics, based on the method of CALPHAD modeling (the calculation of phase diagrams), makes phase diagrams calculations routinely [7, 8]. The CALPHAD method is based on phenomenological models for the Gibbs energy of the all phases in a system. The model parameters are calculated from thermochemical data of individual phases (heat capacity, enthalpy, entropy) and phase equilibrium data between phases. Nevertheless, existing thermodynamic database resources provide a rather limited set of the required information for calculations. There are also many compounds of practical interest which the enthalpy data is known but the entropy data may be uncertain or entirely lacking. The experimental determination of the entropy of materials is difficult and time demanding. In spite of recent progress in first-principles calculations of the entropy [9–11], these calculations, as it was noted in a review [11], have, in many cases, not reached yet the level to be used successfully in CALPHAD modeling. Correlation methods, which may provide estimation of the missing entropy values with reasonable accuracy, can fill this gap. A variety of techniques are presently available for the estimation of standard entropy [12–16]. Atomic masses, molar weight, atomic numbers of elements and molar volumes, as the most accessible physical quantities, are used. One of these, which still largely used, has been developed by Latimer for predominantly ionic compounds [16]. The calculation of the entropy of an ionic inorganic compound is performed by simple summation of the tabulated cationic and anionic contributions into the entropy. The main purpose of this work is to present the correlations between the standard entropy and the reduced mass of a chemical bond for binary compounds and develop predictive schemes for the estimation of standard entropy of binary, ternary, quaternary and higher component sulfides. We propose to use the reduced mass as a correlation parameter taking into account the following:

- the Einstein theory of heat capacity provides a theoretical connection between heat capacity and entropy;
- the Einstein theory relies in the assumption that a single vibration frequency characterizes all $3N$ oscillators;
- the frequency of atomic vibrations is proportional to the square root of the reduced mass of a chemical bond.

The reduced mass, μ , is calculated by:

$$\mu = \frac{m_i m_j}{m_i + m_j}, \quad (1)$$

where m_i and m_j are the atomic masses of atoms i and j forming i – j chemical bond.

RESULTS AND DISCUSSION

Sulfides can be subdivided into four general categories which are commonly identified as mono-sulfides, sesquisulfides, disulfides and complex sulfides composed of different atoms (so called sulfosalts). In this study, the preliminary consideration of relationships between the standard entropy and reduced mass of M–S bond (M = metal atoms) for binary sulfides of MS stoichiometry (M = metal cation) has been used as the basis for the development of a predictive scheme for the assessment of the entropy of ternary, quaternary and higher component sulfides. Using standard entropies of mono-sulfides, taken from various tabulations [17–19], plots were made of S_{298}^0 versus reduced mass (μ) of metal–sulfur (M–S) bond. The values of the reduced mass were calculated by substitution of a metal and sulfur atomic masses into Eq. (1). Typical plots for several mono-sulfides of earth-alkaline and transition metals are shown in Fig. 1.

As can be seen from Fig. 1, the relationships are approximated by series of lines with different slopes having a common intersection with coordinates: Y-axis – $S_{298}^0 \approx 105 \text{ JK}^{-1}\text{mol}^{-1}$; X-axis – $\mu \approx 32.5$. Considering $\mu \approx 32.5$, one can conclude that this value is approximately equal to the molar mass of S^{2-} -ion ($32.07 \text{ g} \cdot \text{mol}^{-1}$). The fact of common intersection availability implies the following simple algebraic form of the correlations:

$$S_{298}^0 = \alpha\mu, \quad (2)$$

where is α fitting constant. Based on this consideration, the values of the constant α for mono-sulfides were determined by the treatment of the available data base [17–19] on standard entropy as follows:

$$\alpha = S_{298}^0 / \mu. \quad (3)$$

The obtained values of the constant α are presented in Table 1 as the mean value for each group of mono-sulfides.

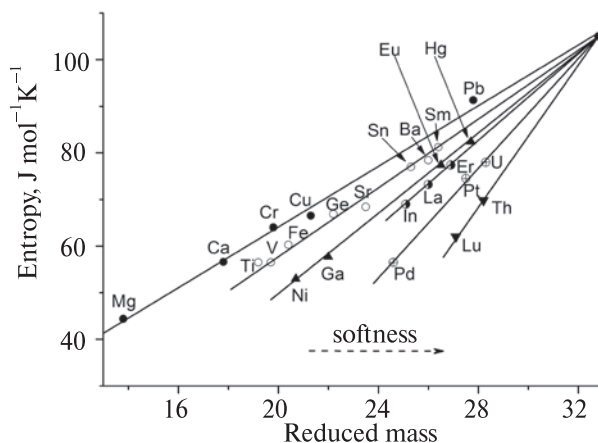


Fig. 1. Standard entropy of mono-sulfides versus reduced mass of M–S bond.

Table 1

Values of constant α for linear relationships between standard entropy, S_{298}^0 ($\text{JK}^{-1}\text{mol}^{-1}$), of mono-sulfides and reduced mass, μ , of M–S bond

Group of mono-sulfides of bivalent cations	Fitted value of constant α ($\text{JK}^{-1}\text{mol}^{-1}$)
Sulfides of Mg, Ca, Cr, Co, Cu, Pb	3.2 ± 0.07
Sulfides of Ti, V, Fe, Ge, Sn, Sr, Ba, the most of lanthanides, Hg	3.0 ± 0.05
Sulfides of Ni, Zn, Ga, Cd, In, U, Pu	2.7 ± 0.05
Sulfides of Rh, Ir, Pd, Pt, Lu, Th	2.4 ± 0.08

It can be seen, analyzing the data in Table 1, that $\alpha = 3.2 \pm 0.07$ coincides approximately with the slope calculated for S^{-2} -ion ($105 : 32.07 = 3.27$) and that the values of constant α are obeying to the simple regularity expressed as $\alpha \approx 3.27 - 0.3n$ ($n = 0, 1, 2, 3$). The differentiation of the mono-sulfides into groups can be interpreted by using the Pearson's concept of hard and soft acids [20]. According to this concept, metal cations are treated as Lewis acids, anions as Lewis bases, and sulfides as Lewis acid-base complexes. The S^{-2} -ion, being soft base, forms more stable complexes (sulfides) with soft cations. Those complexes (with close values of the reduced mass) have lower entropy comparing to the complexes formed by combination of soft base – hard acid. More specifically, the value of entropy is affected by two factors acting in opposite directions: “mass effect” increasing the entropy and the softness of a cation decreasing the entropy (Fig. 1). In Fig. 1, the softness of cations is increased in the direction indicated by the arrow. In order to establish the reliability of the estimations using Eq. (2), the calculated values of the entropy were compared with the reference data [17–19] and the results obtained by the Latimer's method using revised values of the cationic and ionic contributions into entropy [21–23] (Table 2). The appropriate value for metal cation was added to the sulfide ion contribution to calculate the standard entropy of a mono-sulfide (Latimer's method, Table 2).

The sulfide ion contributions into entropy reported by Glasser et al. ($22.1 \text{ JK}^{-1}\text{mol}^{-1}$) [21], Kumok ($27.6 \text{ JK}^{-1}\text{mol}^{-1}$) [22] and Mills ($18.4 \text{ JK}^{-1}\text{mol}^{-1}$) [23] were used. As can be seen from Table 2, both methods reproduce the entropy of mono-sulfides fairly well, but in our case the average deviation ($\pm 2.1 \%$) is lower than that of the Latimer's method ($\pm 3.6 \%$). Note that the errors in the prediction of missing standard entropies, taking into consideration the uncertainties of the constant values, should do not exceed $\pm 3.6 \%$.

In practice, in order to predict the entropy it is desirable to use both methods and formalize the calculation procedure because of the difficulty in defining the group to which a sulfide belongs. As an example, let us consider the estimation of BiS standard entropy. The substitution of the reduced mass of Bi–S bond ($\mu = 27.8$)

Table 2

Results of two methods for estimation of mono-sulfides standard entropy

M	μ of M–S bond	S_{298}^0 (MS) (JK ⁻¹ mol ⁻¹) [17–19]	S_{298}^0 (MS) (JK ⁻¹ mol ⁻¹) Eq. (2)	Deviation (%)	S_{298}^0 (M ²⁺) (JK ⁻¹ mol ⁻¹)	S_{298}^0 (MS) (JK ⁻¹ mol ⁻¹) Latimer's method	Deviation (%)
Mg	13.8	44.4	44.2	-0.5	20.5 [21]	42.6	-4.1
Ca	17.8	56.6 ± 1.3	57.0	0.7	32.5 [21]	54.6	-3.5
Cr	19.8	64.0 ± 8.4	63.4	-0.9	36.4 [22]	64.0	0
Co	20.8	67.4	66.6	-1.2	39.5 [21]	61.6	-8.6
Cu	21.3	66.5 ± 1.7	68.2	2.6	36.5 [22]	64.1	-3.6
Zn	21.5	57.7 ± 0.4	58.0	1.5	37.3 [21]	59.4	2.9
Pb	27.8	91.3 ± 1.2	89.0	-2.5	62.6 [22]	90.2	-1.2
Sr	23.5	68.4 ± 0.8	70.5	3.1	43.0 [22]	70.6	3.2
Ba	26.0	78.4 ± 1.3	78.0	-0.5	55.1 [21]	77.2	-1.5
Ti	19.2	56.5 ± 8.4	57.6	1.9	39.3 [23]	57.7	2.1
V	19.7	56.5	59.1	4.6	36.8 [23]	55.2	-2.3
Fe	20.4	60.3 ± 0.3	61.2	1.5	38.6 [21]	60.7	0.7
Ge	22.2	66.9 ± 0.8	66.6	-0.4	36.7 [22]	64.3	-2.6
Sn	25.3	77.0 ± 0.8	75.9	-1.4	51.9 [22]	79.5	3.2
Cd	24.9	68.2 ± 0.8	67.2	-1.5	46.4 [22]	74.0	8.5
Hg	27.7	82.4 ± 2.1	83.1	0.4	59.4 [23]	77.8	-5.6
La	26.0	73.2	78.0	6.5	42.0 [22]	69.6	-4.9
Ce	26.1	78.2 ± 0.8	78.3	0.1	48.8 [22]	76.4	-2.3
Nd	26.2	77.8	78.6	1.0	60.7 [22]	79.1	1.3
Ni	20.7	53.0 ± 0.3	55.9	5.5	29.6 [21]	51.7	-2.5
Ga	22.0	57.7	59.4	2.9	31.4 [22]	59.0	2.3
In	25.1	69.0 ± 0.4	67.5	-2.2	55.0 [23]	73.4	6.4
Th	28.2	69.8 ± 0.3	67.6	-3.0	47.9 [22]	75.5	8.2
U	28.3	78.0 ± 0.4	76.4	-2.0	53.0 [22]	80.6	3.5
Pu	28.3	78.2	76.4	-2.3	53.5 [22]	81.1	3.7
			Average deviation: ±2.1 %			Average deviation: ±3.6 %	

and the constants α (Table 1) into Eq. (2) gives the following possible values for BiS entropy: 89.0; 83.4; 75.1 and 66.7 JK⁻¹mol⁻¹. Then, the summation of Bi⁺² and S⁻²-ions contributions into the entropy (the value of Bi-cation contribution is 65.0 ± 9.2 JK⁻¹mol⁻¹, Mills' system [23]) yields S_{298}^0 BiS = 83.4 ± 9.2 JK⁻¹mol⁻¹. Thus, the value 83.4 ± 3 JK⁻¹mol⁻¹ can be considered a reliable value of BiS entropy. Further, it was found that Eq. (2) is also valid for description of the relations between the entropy of sesquisulfides (M₂S₃) and disulfides (MS₂), and the reduced mass. The fitted values of constant α are compiled in Tables 3, 4. As in case of monosulfides, the sesquisulfides and disulfides are subdivided into groups. Since S⁻² and S₂⁻²-ions are soft bases, such division can also be interpreted in terms of Pearson's concept [20].

It can be seen from Tables 3 and 4 that the values of constant α form the sequences described as follows: for transition metal sesquisulfides $\alpha = 7.0 - 0.5n$ ($n = 0, 1, 2$); for disulfides $\alpha \approx 4.0 - 0.5n$ ($n = 0, 1, 2, 3, 4$). We compared "μ - based" values of entropy for several disulfides with tabulated data [17–19] and the data obtained using Jenkins and Glasser's method [12, 13]. According to this method, the entropy of solid inorganic compounds can be determined using the following correlation equation:

$$S_{298}^0 = kV_m + c, \quad (4)$$

where V_m is the formula unit volume (nm³), k and c are the specific constants for a given group of compounds.

Table 3

Values of constant α for linear relationships between standard entropy, S_{298}^0 (JK⁻¹ mol⁻¹), of sesquisulfides and reduced mass, μ , of M–S bond

Group of M ₂ S ₃ sulfides	Fitted value of constant α (JK ⁻¹ mol ⁻¹)
Sulfides of As, Sb and Bi	7.2 ± 0.05
Sulfides of U, Pu, the most of lanthanides	7.0 ± 0.1
Sulfides of Ti, Fe, Cr, Ga, In, La, Th	6.5 ± 0.1
Sulfides of Ni, Mo, Rh, Re, Ir	5.5 ± 0.1

Table 4

Values of constant α for linear relationships between standard entropy, S_{298}^0 (JK⁻¹ mol⁻¹), of disulfides and reduced mass, μ , of M–S bond

Group of MS ₂ sulfides	Fitted value of constant α (JK ⁻¹ mol ⁻¹)
Sulfides of Ti, Mn, Ge, U	4.0 ± 0.1
Sulfides of Co, Zr, Sn, Pd, Th	3.5 ± 0.1
Sulfides of Ni, Hf, Nb, Ta, Rh	3.0 ± 0.1
Sulfides of Fe, Mo, W, Ir, Pt	2.5 ± 0.1
Sulfides of Ru, Os, Re	2.2 ± 0.1

In this study, the formula unit volumes of compounds were calculated on the base of density data using the following formula [13]:

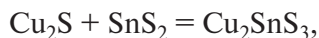
$$V_m = M/602.2\rho, \quad (5)$$

where M is the molar mass ($\text{g} \cdot \text{mol}^{-1}$), ρ is the density ($\text{g} \cdot \text{cm}^{-3}$); 602.2 is the conversion factor between $\text{cm}^3 \cdot \text{mol}^{-1}$ and nm^3 . Plotting of disulfides entropy versus formula unit volume (the density data were taken from [24]) two linear correlation equations were obtained (the plots are not given here). The first correlation fits the available entropy data for disulfides of Ge, W, Mo, Zr, Re and Ru; while the second one fits the entropy data for disulfides of Ti, Fe, Mn, Ni, Co, Sn, Pd, Pt, Ir and Th. The fitting parameters k were found to be 1167 ± 60 and 1385 ± 55 for the first and second correlations, respectively, but the values of the parameter c were obtained in the both cases equal to zero. As it is seen from Table 5, the both equations reproduce fairly well the data on entropy and allow us to evaluate the entropy with the close average deviations.

The reliability and accuracy of disulfides entropy estimations are significantly improved if one combines these two methods. As example, let us consider the prediction of TcS_2 entropy ($\mu = 24.16$, $V_m = 0.0530 \text{ nm}^3$). For this case, in order to formalize the calculation procedure, we suggest the substitution of all values of constant α (Table 4) into Eq. (2) and the constant k values into Eq. (4). By comparing these two series of values, i. e. 109.8, 96.0, 72.5, 68.6 and $53.2 \text{ JK}^{-1}\text{mol}^{-1}$, and 61.8 and $73.4 \text{ JK}^{-1}\text{mol}^{-1}$, one can choose the closest values and take an average, which represents the most reliable value of TcS_2 entropy ($73.0 \pm 2 \text{ JK}^{-1}\text{mol}^{-1}$). We have used this scheme for the estimation of the missing values of entropy for disulfides of V, Cr, Nb, Rh, Os and Hf. The predicted data are:

$$\begin{aligned} S_{298}^0(\text{VS}_2) &= 67.9 \pm 3; \quad S_{298}^0(\text{CrS}_2) = 67.2 \pm 3; \\ S_{298}^0(\text{NbS}_2) &= 72.0 \pm 3; \quad S_{298}^0(\text{RhS}_2) = 70.5 \pm 5; \\ S_{298}^0(\text{OsS}_2) &= 60.3 \pm 5 \text{ and } S_{298}^0(\text{HfS}_2) = 83.0 \pm 4 \text{ JK}^{-1}\text{mol}^{-1}. \end{aligned}$$

We have further extended the application of the obtained correlations for the case of ternary, quaternary and higher component sulfides (sulfosalts) using the additivity principle for entropy [25, 26]. Thus, if we consider the sulfosalts as products of the reactions between binary sulfides, as for instance:



and neglect the change in the entropy of such reactions [25], the following equation for the estimation of the sulfosalts entropy is obtained:

$$S_{298}^0 = \sum_{i=1}^n \alpha_i \mu_i, \quad (6)$$

where the sum covers all binary sulfides, subscribe i is referred to the i -th binary sulfide and $n = 2, 3, 4, \dots$. For the case of Cu_2SnS_3 (mineral mohite), Eq. (5) takes the following expression

$$S_{298}^0 \text{Cu}_2\text{SnS}_3 = \alpha_{\text{Cu}_2\text{S}} \mu_{\text{Cu}_2\text{S}} + \alpha_{\text{SnS}_2} \mu_{\text{SnS}_2}.$$

Table 5

Comparison of two methods for estimation of disulfides standard entropy

M	μ of M–S bond	S_{298}^0 (MS ₂) (JK ⁻¹ mol ⁻¹) [17–19]	S_{298}^0 (MS ₂) (JK ⁻¹ mol ⁻¹) Eq. (2)	Deviation (%)	V_{m^3} (nm ³)	S_{298}^0 (MS ₂) (JK ⁻¹ mol ⁻¹) Eq. (4)	Deviation (%)
Ge	22.2	87.4	88.8	1.6	0.0772	90.1	3.1
Ti	19.2	78.4 ± 0.6	76.8	-2.0	0.0578	80.0	1.8
Mn	20.2	82.0 ± 4	80.8	-1.5	0.0568	78.6	-4.1
Fe	20.4	52.9 ± 0.2	51.0	0.8	0.0397	55.0	4.0
Co	20.8	69.0	72.8	4.0	0.0479	66.3	-3.9
Ni	20.7	72.0 ± 8.4	74.5	-0.8	0.0529	73.3	1.8
Sn	25.3	87.4 ± 0.8	88.6	1.4	0.0675	93.4	6.9
Zr	23.7	78.2	82.9	6.0	0.0667	79.0	1.0
Th	28.2	96.2 ± 0.8	98.7	2.6	0.0674	93.3	-3.0
Ru	24.3	54.4	53.5	-1.7	0.0441	51.5	-5.3
Mo	24.0	62.6 ± 0.1	60.0	4.6	0.0532	62.1	4.4
Ir	27.5	69.0	68.7	-0.3	0.0505	69.9	1.3
Pd	24.6	87.9	86.1	-1.8	0.0585	81.0	7.8
W	27.3	64.9	68.2	5.1	0.0533	62.1	-2.8
Re	27.4	60.7	60.2	-0.8	0.0554	64.6	6.4
Pt	27.5	74.7 ± 0.2	68.8	-7.9	0.0562	77.8	4.1
Ta	27.2	75.3	81.6	8.4	0.0560	77.6	3.0
Zr	23.7	78.2	82.9	6.0	0.0667	79.0	1.0
			Average deviation: ±3.0 %			Average deviation: ±3.8 %	

Eq. (6) can be considered as a specific form of the constituent additivity method [25, 26]. Undoubtedly, the summation of reference data or data from original works on entropy is, as it assumes the constituent additivity method, a simpler procedure than the use of Eq. (6). However, entropy data for binary sulfides is often difficult to extract from the scattered information, and the data can be uncertain or entirely lacking. We compared the results of sulfosalts entropy evaluation within Eq. (6) with the data obtained by applying Eq. (4). The formula unit volumes of sulfosalts were determined using density data from [27], but the values of constants $k = 1579 \pm 30$ and $c = 6 \pm 6$ were taken from [13]. Table 6 shows the results of the application of two methods. It is seen from Table 6, in most cases the fairly well agreement between data of the two methods is observed. More specifically, when binary constituents possess close acid–base properties, e. g. FeFe_2S_4 , NiNi_2S_4 , PbSnS_2 , PbCuBiS_3 , CuRh_2S_4 , FeSb_2S_4 and ZnCr_2S_4 , an excellent agreement between results of two methods is observed.

In this work, the square root of the ionic potential of a cation, $\Phi = \sqrt{Z/r}$ (where Z is charge and r is radius of a cation) [35], has been used as the simplest measure of the acidity of a binary compound. For the above-mentioned sulfides, the difference between acid-base properties of the constituents, $\Delta\Phi$, does not exceed 0.5.

Table 6

Results of two methods of the entropy evaluation for several ternary and higher component sulfides (sulfosalts)

Sulfide (mineral)	Developed formula of the sulfide	V_m (nm ³)	Standard entropy (JK ⁻¹ mol ⁻¹)		
			Eq. (6)	Eq. (4)	Expt. value
FeFe_2S_4 (greigite)	$\text{FeS} \cdot \text{Fe}_2\text{S}_3$	0.1213	194	197	—
NiNi_2S_4	$\text{NiS} \cdot \text{Ni}_2\text{S}_3$	0.1075	172	176	—
CuFeS_2	$\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$	0.0726	127	121	124.9 ± 3 [32]
PbSnS_2 (teallite)	$\text{PbS} \cdot \text{SnS}$	0.1018	165	167	—
PbCuBiS_3 (aikinite)	$\text{PbS} \cdot \text{CuS} \cdot \text{BiS}$	0.1485	241	240	—
CuInS_2	$\text{Cu}_2\text{S} \cdot \text{In}_2\text{S}_3$	0.0849	142	140	137.2 ± 1 [28]
CuRh_2S_4	$\text{CuS} \cdot \text{Rh}_2\text{S}_3$	0.1205	203	196	—

The end of the table 6

Sulfide (mineral)	Developed formula of the sulfide	V_m (nm ³)	Standard entropy (JK ⁻¹ mol ⁻¹)		
			Eq. (6)	Eq. (4)	Expt. value
CuCoPtS ₄	CuS · CoS · PtS ₂	0.1141	204	186	—
Pb ₅ Sb ₄ S ₁₁	5PbS · 2Sb ₂ S ₃	0.5016	811	798	—
FeSb ₂ S ₄ (berthierite)	FeS · Sb ₂ S ₃	0.1531	242	248	245.0 ± 0.1 [29]
Cu ₂ SnS ₃ (mohite)	Cu ₂ S · SnS ₂	0.1169	209	190	196.3 ± 19 [30]
Pb ₅ Sn ₃ Sb ₂ S ₁₄	5PbS · 3SnS ₂ · Sb ₂ S ₃	0.5887	894	936	—
ZnCr ₂ S ₄ (kalininite)	ZnS · Cr ₂ S ₃	0.1222	198	199	—
Pb ₄ FeSb ₆ S ₁₄	4PbS · FeS · 3Sb ₂ S ₃	0.6089	966	967	—
CuBiS ₂ (empelectite)	Cu ₂ S · Bi ₂ S ₃	0.0874	161	144	156 ± 12 [30]
α-AgBiS ₂ (matildite)	Ag ₂ S · Bi ₂ S ₃	0.0928	171	152	171.9 ± 18 [31]
β-AgBiS ₂ (matildite)	Ag ₂ S · Bi ₂ S ₃	0.0905	171	149	156.9 ± 5 [32]
α-AgSbS ₂	Ag ₂ S · Sb ₂ S ₃	0.0931	162	153	157.4 ± 3 [33]
AgBi ₃ S ₅ (pavonite)	Ag ₂ S · 3Bi ₂ S ₃	0.2195	371	353	372.7 ± 2.8 [34]

However, in other cases, $\Delta\Phi$ is larger than 0.5 and can reach 1.2. We believe that Jenkins and Glasser's method [12, 13] gives more reasonable data for sulfosalts formed by the reaction of "strong base – strong acid" since the formation of complex anions decreases the total number of particles in the system causing a negative deviation from the sum of molar volumes of binary sulfides, and thereby could reduce the entropy (if other factors do not intervene). The experimental data for CuFeS₂, AgBiS₂, AgSbS₂ and AgBi₃S₅ (Table 6) seem to support this suggestion. Thus, the combination of two methods is a good approach for the prediction of standard entropy of ternary, quaternary and higher component sulfides.

CONCLUSIONS

The available reference data and the data from original works on the standard entropy of binary sulfides have been treated in a systematic approach through the correlations between entropy and the reduced mass of the chemical bonds. Regularities that connect the fitting constants of groups of similar compounds have been revealed. On the base of the obtained correlations, simple and well defined predictive schemes are proposed. The mean deviations of the standard entropy estimations from experimental and/or tabulated data using new techniques are in the range of $\pm(1-5)$ %. It was shown that the developed approach in combination with Jenkins and Glasser's method, give reliable values of standard entropy for metal disulfides and complex sulfides (sulfosalts).

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