



# Heat capacity and thermodynamic functions of sphalerite: Implication to sulfide solid-state galvanic cell measurements



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## ARTICLE INFO

### Article history:

Received 12 March 2016

Received in revised form 30 July 2016

Accepted 6 August 2016

Available online 8 August 2016

### Keywords:

Sphalerite

β-ZnS

Heat capacity

Thermodynamic properties

Sulfides

Solid-state galvanic cell

Electromotive force experiment

## ABSTRACT

New adiabatic calorimeter measurements of heat capacity of sphalerite from 13.23 to 312.85 K at ambient pressure agree well with previous adiabatic calorimeter results but overestimate PPMS-derived data (Cardona et al., 2010) at  $T > 150$  K. The adiabatic calorimeter low-temperature heat capacity data and drop-calorimetric high-temperature data on  $H^0(T) - H^0(298.15)$  are rationalized in the framework of the Kieffer-type vibrational spectrum model accounting for dependence of vibrational frequencies on volume and temperature. Thermodynamic properties of sphalerite are calculated by the elaborated model from 0 to 1300 K.

Present calorimetric results conform to those from high-temperature electromotive force (EMF) experiments (Osadchii et al., 2015) using the Cu/Cu<sub>2</sub>S buffer. The disagreement with data based the Ag/Ag<sub>2</sub>S buffer is explained by deviation of silver sulfide from stoichiometry in the EMF experiments. A correction to the Gibbs energy of formation obtained in high-temperature EMF experiments using the Ag/Ag<sub>2</sub>S buffer is suggested.

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## 1. Introduction

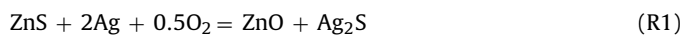
Thermochemical studies of sphalerite β-ZnS(cubic) has rich and long history taking its origin in XIX century [1]. Modern thermodynamic data on sphalerite are mainly based on three studies by [2–4]. Stuve [3] measured heat capacity from 5.62 to 300.1 K by adiabatic calorimetric technique. Birch [4] studied the heat capacity in the liquid helium temperature range between 2.452 and 11.44 K. Modern estimation of standard heat capacity and entropy in popular handbooks [1,5] are based on these studies. Pankratz and King [2] measured high-temperature enthalpy of sphalerite by drop-calorimetry in the range from 402.2 to 1301.1 K. They suggested following equations for standard  $H^0(T) - H^0(298.15)$  and  $C_p^0(T)$  validating for the range studied:

$$\{H^0(T) - H^0(298.15)\}/(\text{J mol}^{-1}) = -16544 + 49.25 T / \text{K} + 2.636 \times 10^{-3}(T/\text{K})^2 + 4.853 \times 10^5(T/\text{K})^{-1} \quad (1)$$

$$C_p^0(T)/(\text{JK}^{-1} \text{mol}^{-1}) = 49.25 + 5.272 \times 10^{-3} T / \text{K} - 4.853 \times 10^5(T/\text{K})^{-2} \quad (2)$$

where  $T$  is the absolute temperature;  $H$  is enthalpy;  $C_p$  is the isobaric heat capacity; hereafter the superscript o denotes that a physical quantity is measured at the standard pressure 10<sup>5</sup> Pa. Eqs. (1) and (2), being extrapolated to low temperatures do not agree with the heat capacity measurements in [3,4]. Recently, Cardona et al. [6] measured the heat capacity of sphalerite in a wide range from 3.5 to 1100 K. Therewith, the measurements were conducted by relaxation calorimeter technique using the Physical Property Measurement System (PPMS) between 3.5 and 326.4 K and by the differential scanning calorimeter (DSC) method at the higher temperatures. Cardona et al's results [6] differ substantially from those in [2,3] at  $T > 150$  K.

The standard Gibbs energy of formation and the Gibbs energy function of sphalerite were recently determined in high-temperature electromotive force (EMF) experiments [7]. The experiments used solid-state galvanic cell and based on following reactions involving Ag/Ag<sub>2</sub>S or Cu/Cu<sub>2</sub>S buffers:

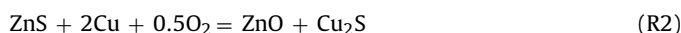


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**Table 1**Heat capacity ( $C_p^0$ ) of sphalerite ( $\beta$ -ZnS) in the range from 13.23 K to 312.85 K at pressure ( $0.1 \pm 0.002$ ) MPa.

T/K <sup>a</sup>	$C_p^0/(\text{JK}^{-1} \text{mol}^{-1})^b$	T/K <sup>a</sup>	$C_p^0/(\text{JK}^{-1} \text{mol}^{-1})^b$	T/K <sup>a</sup>	$C_p^0/(\text{JK}^{-1} \text{mol}^{-1})^b$	T/K <sup>a</sup>	$C_p^0/(\text{JK}^{-1} \text{mol}^{-1})^b$
13.23	0.1984	61.72	15.17	125.61	30.87	214.65	41.55
16.01	0.5445	64.45	15.93	129.43	31.59	219.66	41.93
17.97	1.0250	67.18	16.76	133.29	32.28	224.69	42.27
19.61	1.5530	69.70	17.39	137.15	32.90	230.00	42.62
21.54	2.093	72.52	18.20	141.04	33.52	235.27	42.91
23.46	2.680	75.26	18.97	144.93	34.17	240.27	43.24
25.99	3.508	77.99	19.74	149.88	35.06	245.33	43.69
28.89	4.520	80.73	20.47	155.67	35.74	250.45	43.78
31.66	5.487	83.59	21.24	159.17	36.12	258.21	44.25
34.78	6.600	86.48	22.17	164.00	36.77	263.65	44.40
37.93	7.702	91.62	23.27	168.93	37.35	269.02	44.71
41.05	8.761	95.13	24.19	173.91	37.96	274.56	44.99
44.22	9.788	98.85	25.12	178.77	38.48	280.13	45.24
47.06	10.713	102.42	26.14	184.05	38.90	285.72	45.48
51.43	12.16	106.06	26.79	189.40	39.43	291.19	45.73
53.49	12.83	109.93	27.68	194.40	39.95	297.09	45.70
55.51	13.31	113.87	28.52	199.39	40.39	304.72	46.14
57.50	14.00	117.79	29.35	204.53	40.77	312.85	46.50
59.41	14.51	121.86	30.17	209.77	41.20		

<sup>a</sup> Uncertainty in temperature measurements do not exceed 0.01 K (0.68 level of confidence).<sup>b</sup> Relative standard uncertainties (0.68 level of confidence) in  $C_p^0$  are 1.2% at temperatures below 40 K; 0.32% at temperatures between 40 and 150 K; and 0.17% at temperatures above 150 K.

A noticeable difference in the temperature dependence of the standard Gibbs energy of sphalerite was observed between the EMF experiments involving Ag/Ag<sub>2</sub>S (R1) and Cu/Cu<sub>2</sub>S (R2) buffers [7].

In the present paper, we have verified data on the heat capacity in the low temperature range (from 13.23 to 323.85 K) and conformed the low-temperatures measurements and high-temperature data [2] based on the model vibration spectrum and taking into account its explicit dependence on temperature. Comparing the standard Gibbs energy functions of reactions (R1) and (R2) obtained from calorimetric data with those obtained in the EMF measurements [7], we have discussed a possible reason of the difference in temperature dependence of the standard Gibbs energy of sphalerite mentioned above and provided recommendations on usage of the Ag/Ag<sub>2</sub>S buffer in high-temperature EMF experiments.

## 2. Experiments and results

### 2.1. Heat capacity measurements

We measured the standard heat capacity of sphalerite in the temperature range from 13.23 to 312.85 K. This range is a key one for estimating the standard heat capacity, entropy and enthalpy change  $H^0(298.15) - H^0(0)$ .

We investigated a sphalerite produced commercially by the “Alfa Aesar”. It represents a light yellow fine powder containing 99.99 mass% of the major component. X-ray diffraction analysis showed absence of wurtzite  $\alpha$ -ZnS in the specimen. Measurements of the heat capacity of sphalerite were conducted using the adiabatic calorimeter designed and assembled in the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences. Its construction is described briefly in the Appendix A (see also the detailed description in [8]). In the Appendix A, one can also find results of measurements of empty calorimetric ampoule and tests of the calorimeter using standard reference material, benzoic acid. The sphalerite sample weight was  $(3.57725 \pm 0.00004)$  g. The molecular mass was accepted  $(97.4340 \pm 0.0001)$  g mol<sup>-1</sup> [9].

Results of our heat capacity measurements of sphalerite are presented in Table 1. One can observe a good agreement between present (Table 1) and previous adiabatic calorimetric data [3] (Fig. 1). Extrapolation of our data to the absolute zero according to the  $T^3$  law shows agreement of our measurements with

those by Birch [4]. The PPMS relaxation calorimetric results [6] lie successively lower than the adiabatic calorimetric measurements data at  $T > 150$  K (Fig. 1). Such deviation between PPMS and adiabatic calorimeter measurements is not exclusive for present measurements and was observed earlier [10]. Nevertheless, the difference between our adiabatic calorimetric and the PPMS data [6] does not exceed accuracy warranted by PPMS technique (2% at  $5 \text{ K} < T < 300 \text{ K}$ ) [11].

### 2.2. Mathematical treatment and rationalization of experimental data

We rationalized the experimental data based on the Kieffer-type model vibrational spectrum [12]. According to Kieffer [12], one can rationalize heat capacity and other thermodynamic function in the harmonic (quasiharmonic) approximation using a model spectrum (density of states) consisting of three acoustic branches, one or several optic continuums and one or several Einstein oscillators (see Fig. 1 in Kieffer’s paper [12]). The acoustic branch is designed analogously to the vibrational spectrum of a linear crystalline chain. The optic continuum represents the uniform density of states between low- and high-boundary frequencies. The isochoric heat capacity is expressed in the framework of this model as:

$$\frac{zC_V(T)}{R} = \sum_j a_j^S S(\theta_j^S/T) + \sum_i a_i^K K(\theta_i^{KL}/T, \theta_i^{KU}/T) + \sum_l a_l^E E(\theta_l^E/T) \quad (3)$$

where  $C_V$  is the isochoric heat capacity;  $R$  is the universal gas constant;  $z$  is the number of molecules in the primitive Bravais cell ( $z = 1$  for sphalerite);  $\theta_j^S$ ,  $\theta_i^{KL}$ ,  $\theta_i^{KU}$  and  $\theta_l^E$  are the characteristic temperatures for the  $j$ -th acoustic branch, the  $i$ -th optic continuum and the  $l$ -th Einstein oscillator, respectively. These characteristic temperatures relate to appropriate boundary frequencies of acoustic branches and optic continuum and to frequencies of the Einstein oscillators by the equation:  $\theta = h\nu/k$  ( $h$  and  $k$  are Planck’s and Boltzmann’s constants;  $\nu$  is appropriate frequency). Functions  $S$ ,  $K$  and  $E$  are defined as follows [12]:

$$S(x) \equiv \left(\frac{2}{\pi}\right)^3 \int_0^x \frac{\arcsin^2(\xi/x) \xi^2 \exp(\xi)}{(x^2 - \xi^2)^{1/2} (\exp(\xi) - 1)^2} d\xi \quad (4)$$

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