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Electrochemical determination of the thermodynamic parameters of sphalerite, ZnS

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ABSTRACT

Thermodynamic properties of sphalerite (β-ZnS, F4-3m) were studied by the method of high-temperature galvanic cell with separate gas space and Y_2O_3-stabilized ZrO_2 as solid-state electrolyte. The temperature dependences of the cell electromotive force (EMF) were obtained for the reaction

$$ZnS + 2Ag + NiO = ZnO + Ag_2S + Ni$$

in the temperature range 782–1050 K, and for the reaction

$$ZnS + 2Cu + NiO = ZnO + Cu_2S + Ni$$

in the temperature range 848–1288 K.

The standard parameters of sphalerite were analyzed by the second law of thermodynamics. The standard enthalpy of formation of ZnS, $\Delta_f H^o_{ZnS}(298\ K) = -201.07 \pm 1.3$ kJ mol^{-1}, was calculated for the reaction $Zn_{(s)} + S_{(s)} = ZnS_{(\beta)}$ using the third law of thermodynamics (Gef method) and data on standard enthalpy of formation for ZnO, NiO, Ag_2S, and Cu_2S. From the EMF results for the ZnS/ZnO equilibrium and using the known data on free energy of formation of ZnO, NiO, Ag_2S and Cu_2S, the free energy of sphalerite formation was found according to the reaction $Zn_{(l)} + 0.5S_{2(g)} = ZnS_{(\beta)}$:

$$\Delta_f G^o_{ZnS}(T) \pm 1000\ \text{J mol}^{-1} = -273,870 + 107.30 \cdot T, (782 < T/\text{K} < 1050), (\log fS_2 > -9)$$

$$\Delta_f G^O_{ZnS}(T) \pm 1300\ \text{J mol}^{-1} = -268,892 + 102.67 \cdot T, (848 < T/\text{K} < 1180), (\log fS_2 < -9)$$

Similarly, for the reaction $Zn_{(g)} + 0.5S_{2(g)} = ZnS_{(\beta)}$:

$$\Delta_f G^o_{ZnS}(T) \pm 1300\ \text{J mol}^{-1} = -382,203 + 198.75 \cdot T, (1180 < T/\text{K} < 1293)$$

The obtained results were compared to the literature data.

1. Introduction

Sphalerite, with its cubic modification $ZnS_{(\beta)}$ stable below 1020 °C (1293 K), is the main industrial source of metallic zinc, especially common in the polymetallic sulfide ores. Sphalerite is also found in black smokers, iron meteorites, and as an accessory mineral in very diverse geological formations.

Natural sphalerite is most typically present as the replacement solid solution. Zinc is replaced by other divalent metals, such as Fe Mn, Cd, In, Ge and Hg, some of which are present in commercial amounts (In, Cd, Ge). Also, the Zn–Fe solid solution can be used as a geological barometer [1–3].

Numerous studies of the thermodynamic properties of pure sphalerite include EMF-experiments [4–6], calorimetric measurements [7,8], and computer models of sphalerite structure [9,10]. The EMF experiment presented in this study is similar to that described in [6] and [5], but it was performed at much lower fugacities of sulfur and oxygen, which were buffered by the Ag/Ag_2S, Cu/Cu_2S, and Ni/NiO mixtures. Agreement of the data

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obtained with different solid-state buffers was taken as the criterion for consistency of thermodynamic properties of all reactants and products in the above-mentioned reactions.

2. Methods

2.1. Thermodynamic background

The reactions considered in this study are graphically presented on the phase diagram in Fig. 1.

As seen from Fig. 1, the ZnS/ZnO equilibrium is monovariant at constant temperature and pressure, i.e. it is only determined by the partial pressures of O_2 and S_2, and can be expressed through the following equation:

$$ZnS + 0.5O_2 = ZnO + 0.5S_2 \quad (R1)$$

For measuring experimentally the partial pressure of oxygen, the partial pressure of sulfur must be fixed. In some previous studies [4–6], the partial pressure of sulfur was maintained by the SO_2 gas flow (pSO_2 = 1 atm), which was passed through the cell during EMF measurements. In the present study, the sulfur pressure was buffered by Ag/Ag_2S and Cu/Cu_2S mixtures, according to the following reactions:

$$2Ag + 0.5S_2 = Ag_2S \quad (R2)$$

$$2Cu + 0.5S_2 = Cu_2S \quad (R3)$$

Reactions (R2) and (R3) are shown in Fig. 1 as horizontal dashed lines. Combination of these reactions with the ZnS/ZnO equilibrium (R1) result in invariant equilibria, which at constant temperature only depend on the partial pressure of oxygen. In Fig. 1, these invariant conditions are shown by the intersection points of the Ag/Ag_2S and Cu/Cu_2S lines with the ZnS/ZnO line. Respectively, the resulting reactions can be therefore given as

$$ZnS + 2Ag + 0.5O_2 = ZnO + Ag_2S \quad (R4)$$

$$ZnS + 2Cu + 0.5O_2 = ZnO + Cu_2S \quad (R5)$$

Using a solid electrolyte with O^{2-} conductivity makes it possible to determine the difference of the partial pressures of oxygen between the target reactions, (R4) and (R5), and the reference system (Ni/NiO):

$$Ni + 0.5O_2 = NiO \quad (R6)$$

The EMF measurements were performed in separate-gas-space electrochemical Cells (A) and (B), as described below:

$$Pt\,|\,ZnS, ZnO, Ag_2S, Ag, p(O_2, R4)\,|\,YSZ\,|\,Ni, NiO, p(O_{2ref})\,|\,Pt \quad (A)$$

$$Pt\,|\,ZnS, ZnO, Cu_2S, Cu, p(O_2, R5)\,|\,YSZ\,|\,Ni, NiO, p(O_{2ref})\,|\,Pt \quad (B)$$

Y_2O_3-stabilized ZrO_2 (YSZ) was used as a solid electrolyte for these cells.

The partial pressures of oxygen in each cell are different on the left and on the right side from the YSZ, which results in the potential difference (EMF) on the inert platinum electrodes according to the reaction:

$$0.5O_2 + 2e^- = O^{2-} \quad (R7)$$

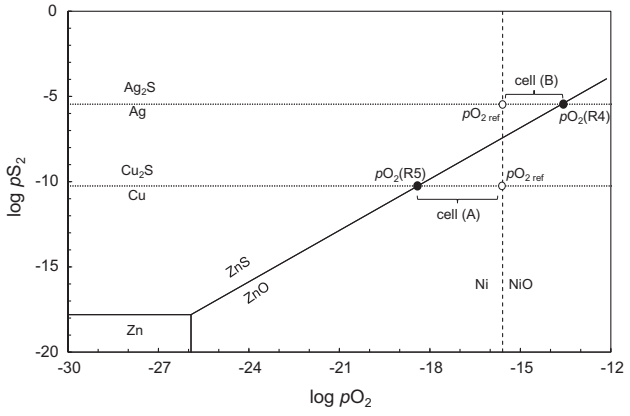

Fig. 1. Phase equilibria in the Zn–Ag–S–O and Zn–Cu–S–O systems at 1000 K and total pressure of 1 bar. Positions of reactions (R4) and (R5) relatively to Ni/NiO oxygen buffer are shown (see text).

The ratios of the oxygen partial pressures (R6)/(R4) and (R6)/(R5) are the thermodynamic constants of the following reactions under study:

$$ZnS + 2Ag + NiO = ZnO + Ag_2S + Ni \quad (R8)$$

$$ZnS + 2Cu + NiO = ZnO + Cu_2S + Ni \quad (R9)$$

which are directly related to the EMF (E) in Cells (A) and (B), respectively. The total potential forming process corresponds to the differences R4, R5, R6, (R5) and (R6), i.e. reactions (R8) and (R9).

Applying the main equation of thermodynamics, $\Delta_rG(T) = -n \cdot F \cdot E(T)$, to this system, we obtain:

$$\Delta_rG^o(T) = -n \cdot F \cdot E(T)\ 10^{-3} = R \cdot T \cdot \ln 10 \cdot \log(pO_2/pO_{2ref}) \quad (8)$$

where $n = 2$ is the number of electrons in the electrode reaction (R7), F = 96,485 C/mol is the Faraday constant, $E(T)$ is the cell EMF (mV), T is absolute temperature (K), $pO_{2\,ref}$ is the oxygen partial pressure in the reference system (R6), pO_2 is the oxygen partial pressure in the sample system, specifically in reactions (R4) or (R5).

If the internal impedance of the voltmeter is several orders of magnitude higher than the impedance of the cell, the open circuit condition can be assumed. In this case, the maximum potential difference (EMF) can be measured and further translated into the ratio of oxygen partial pressures between the sample and reference systems. Finally, the standard Gibbs energy can be found from the oxygen partial pressure data for the studied reaction.

Furthermore, the EMF method allows the heat and entropy effects to be found for reactions (R8) and (R9), as follows:

$$\Delta_rS = n \cdot F \cdot (dE/dT) \cdot 10^{-3} \quad (9)$$

$$\Delta_rH = -n \cdot F \cdot [E - (dE/dT) \cdot T]\ 10^{-3} \quad (10)$$

2.2. Chemicals and synthesis procedure

Chemical reagents for this study included silver powder (99.95%), copper powder (99.99%), nickel powder (99.95%), crystalline sulfur (99.995%), ZnO (99.99%), NiO (99.9%), and Ag_2S (99.9%).

Copper sulfide was synthesized by solid-phase synthesis at 200 C from metallic copper and crystalline sulfur, which were sealed in evacuated silica glass capsules.

Zinc sulfide (Aldrich, 99.9%) used in this study was in the form of aggregates of fine crystalline powder 3–12 mm in size, white in color with a slight yellow tint. The X-ray diffraction analysis performed on Bruker 8 (advance Kα_1, λ = 1.54056 Å) indicated complete correspondence with the JCPDS X-ray card 05-0566. The chemical was tested for the presence of adsorbed water and excess sulfur. For this test, 1 g of ZnS was placed in a long silica glass capsule, which was evacuated and sealed in the oxygen flame at the residual pressure of approximately 10^{-3} Torr. The loaded end of the capsule was held in the tube resistance furnace at 873 K, while the other free end was kept at room temperature. After keeping this capsule at such conditions for 24 h, no traces of condensed matter was found at its cold end.

2.3. Electrochemical cell design

The principle schematic of the separate-gas-space EMF-cell is shown in Fig. 2.

The cell consists of two parts: sample system (12) and reference system (13), which are divided by the solid electrolyte (7). The cell was assembled in the following way. The reference system mixture, i.e. Ni/NiO, was loaded into the closed-end YSZ tube, and a reference electrode (2) was dipped into the mixture. The ceramic holder of the reference electrode has a hole (6) that prevents the powder from being sucked out during evacuation. Then a small silica glass tube was glued with epoxy on the open end of the YSZ tube was later used for reference system evacuation. As the next step a Pt wire was wound around the lower end of the YSZ tube to make the inert sample electrode. The YSZ assembly was further inserted into the larger silica glass tube (4), which contained the sample mixture. A thin plug of kaoline wool (14) placed on the bottom of the tube provides some tolerance for thermal expansion of the YSZ and thereby prevents break in the epoxy seal (3) in the course of the high temperature experiment. The volumes of the reference and sample systems of the cell were evacuated at the residual pressure of 10^{-3} Torr and sealed in the oxygen flame.

Before loading the cell, the components of the reference and sample systems were thoroughly mixed in an agate mortar in the proportions corresponding to the stoichiometry of the reaction under study. The total amounts of the reagents were based on the consideration for the most complete contact of the powders with the Pt-electrodes. The height of the working zone of the EMF-cell ranged from 16 to 20 mm.

2.4. EMF measurements

The EMF-cell was heated in a vertical resistance furnace with an isothermic zone longer than 20 mm. Temperature was maintained by a temperature controller to ±0.3 K and a Pt/Pt-thermocouple (10 wt.% Rh), which was placed along the