DETERMINATION OF $\Delta_f G^{\circ}_T$ **OF SPHALERITE BY EMF METHOD WITH Ag/Ag₂S AND Cu/Cu₂S SOLID-STATE GAS BUFFERS Rappo O.A.** (IEM RAS), **Osadchii E.G.** (IEM RAS)

euo@iem.ac.ru

 $\Delta_{\rm f} G^{\rm o}_{\rm T}$ of sphalerite was determined by high temperature electrochemical method by using YSZ solid electrolyte with oxygen ion conductivity. The phase relations in the Zn-Cu/Ag-S-O system at 1000 K are shown in Fig.1.



Fig.1. Phase relations in the Zn-Cu/Ag-S-O system at 1000 K.

Oxygen partial pressures in the following phase reactions:

ZnS(s)+2Ag(s)+1/2O₂(g)=ZnO(s)+Ag₂S(s)(I), ZnS(s)+2Cu(s)+1/2O₂(g)=ZnO(s)+Cu₂S(s)(II) have been investigated via electromotive force (EMF) measurements in solid-state galvanic cells with yttria stabilized zirkonia (YSZ) as a solid electrolyte (Ni/NiO reference system): Pt|Ni,NiO|YSZ|ZnS,ZnO,Ag,Ag₂S,O₂|Pt (A), Pt|Ni,NiO|YSZ|ZnS,ZnO,Cu,Cu₂S,O₂|Pt (B). Cu/Cu₂S and Ag/Ag₂S auxiliary systems were used to stabilized $p(SO_2)$ in reactions (I/II).

Experiment conditions

The cells were placed into the isothermal (at least 20 mm in height) zone of a vertical resistance (direct current) furnace (18 mm ID and 250 mm high). The temperature was maintained constant within \pm 0.1 K by the electronic temperature controller "PROTHERM-100" and measured in the middle of the cell with the accuracy of \pm 0.1 K using a K-type thermocouple. The thermocouples

were calibrated against a standard Pt thermometer in a water ultrathermostat. Both, the temperature and the EMF measurements were carried out automatically with the accuracy of (0.01 ± 0.005) mV with a multi-channel millivoltmeter and recorded using a computer data acquisition system. High-input impedance (~ $10^{13} \Omega$) channels were used for the EMF measurements.

The measurements were performed as a "temperature titration". Temperature was changed in 5-10 K steps, and at every temperature value the EMF of the cell was monitored until the equilibrium EMF value was reached. The reversibility of the equilibrium was checked by performing upward and downward temperature changes. The equilibrium was assumed, when the EMF remained unchanged within ± 0.03 mV for at least 12 hours.

Phase composition of the sample systems was confirmed by XRD analysis after experiments. All parts of the cells after the completion of all the experiments were in the same state as before loading. It should be pointed out that the solid electrolyte remained in a very good condition after the EMF experiments.

Results and Calculations

A distinct reversible phase transition of the first order was observed using the Ag/Ag₂S buffer (reaction I) at high $p(SO_2)$ at 1053 K.

The EMF(mV) values measured in Cell A as a function of temperature can be described as follows: $E(A)=-349,23+0,269 \cdot T/K, R^2=0,9999, (782,4 < T/K < 1053,1),$

 $E(A)=-406,91+0,324 \cdot T/K$, R²=0,9997, (1053,1<T/K<1109,9). For the condition $\Delta_r C_p=0$. $\Delta_{trs}H=(5590 \pm 100) \text{ J/mol.}$ At low $p(SO_2)$ (while using the Cu/Cu₂S buffer) a not very distinguishable phase transition appears at 1157 K. However the distinct sphalerite-wurtzite transition was clearly observed at (1293+/-1) K that is in excellent agreement with literature data.

The EMF(mV) values measured in Cell B as a function of temperature can be described as follows: $E(B)=-101,94+0,262 \cdot T/K, R^2=0,9996, (848,5 < T/K < 1144,3),$

 $E(B)=-89,78+0,251 \cdot T/K, R^2=0,9998, (1144,3<T/K<1308,9)$. For the condition $\Delta_r C_p=0$. $\Delta_{trs}H=(1200\pm150) J/mol.$

The EMF values obtained in the experiment are shown in Fig.2.



Fig.2. *E*/mV-*T*/K dependencies for cells (A) and (B), and for cell (B) with 1 degree step at 1035-1059 K (individual measurements).

Calculation of $\Delta_f G^o{}_T$ values

The equilibrium EMF value (E/mV) is related to the sample (pO_2/atm) and the reference oxygen pressure ($p*O_2/atm$), and the temperature (T/K) through the relationship:

 $\log pO_2 = \log p^*O_2 - (n \cdot F \cdot E \cdot 10^{-3})/(R \cdot \ln 10 \cdot T)$ (1), where the amount of electrons is n=4; *E* is the EMF measured/mV; F is the Faraday constant, 96484,56 colomb/mol; R is the gas constant, 8,31 J·K⁻¹·mol⁻¹; *T* is the absolute temperature/K.

Under the conditions of thermodynamic equilibrium $\Delta_{r}G^{o}{}_{T}(I/II) = -\ln 10 \cdot R \cdot T \cdot \log K \qquad (2),$ where $K(I/II) = 1/pO_{2}(I/II)^{\frac{1}{2}}$ (3) Insertion of eqn. (3) into eqn. (2) and a subsequent rearrangement gives: $\Delta_{r}G^{o}{}_{T}(I/II) = \frac{1}{2}\ln 10 \cdot R \cdot T \cdot \log p(O_{2})$ (4). According to the equation (I/II): $\Delta_{f}G^{o}{}_{T}(ZnS) = \Delta_{f}G^{o}{}_{T}(ZnO) + \Delta_{f}G^{o}{}_{T}(Cu_{2}S)/\Delta_{f}G^{o}{}_{T}(Ag_{2}S) - \Delta_{r}G^{o}{}_{T}(I)/\Delta_{r}G^{o}{}_{T}(II)$ (5), where $\Delta_{f}G^{o}{}_{T}(ZnO)$ and $\Delta_{f}G^{o}{}_{T}(Cu_{2}S)$ values were taken from the thermochemical data [1]. $\Delta_{\rm f} G^{\rm o}_{\ T}({\rm ZnS})/{\rm kJ\cdot mol^{-1}(I)} = 0.0001 \cdot T^2 - 0.163 \cdot T - 136.67, \ {\rm R}^2 = 0.9987, \ (848.5 < T/{\rm K} < 1308.9), \\ \Delta_{\rm f} G^{\rm o}_{\ T}({\rm ZnS})/{\rm kJ\cdot mol^{-1}(II)} = 0.0001 \cdot T^2 - 0.137 \cdot T - 153.1, \ {\rm R}^2 = 0.9991, \ (782.4 < T/{\rm K} < 1052.6), \\ \Delta_{\rm f} G^{\rm o}_{\ T}({\rm ZnS})/{\rm kJ\cdot mol^{-1}(II)} = 0.0001 \cdot T^2 - 0.135 \cdot T - 151.76, \ {\rm R}^2 = 1, \ (1052.6 < T/{\rm K} < 1109.9).$

Reference

1. Barin I. Thermochemical Data of Pure Substances, VCH, 1989. 1885p.

Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(22) 2004 Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2004 URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2004/informbul-1_2004/mineral-14e.pdf Published on July, 1, 2004

© Herald of the Department of the Earth Sciences RAS, 1997-2004 All rights reserved