DETERMINATION OF $\Delta_f G^o_T$ OF SPHALERITE AND ZnS ACTIVITY IN $(Fe_{0,3}Zn_{0,7})S$ SOLID SOLUTION BY SOLID-STATE GALVANIC CELL.

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Herald of the Earth Sciences Department RAS, № 1(20)′2002
URL: *http://www.scgis.ru/russian/cp1251/h_dgggms/1-2002/informbul-1.htm#term-13.engl*

Partial oxygen pressures were determined by the high-temperature galvanic cell method using a solid-state electrolyte with oxygen-ion conductivity for the following equilibria:

$$ZnS_{(s)} + 2Cu_{(s)} + \tfrac{1}{2}O_{2(g)} = ZnO_{(s)} + Cu_2S_{(s)} \qquad \text{(I)},$$
$$ZnS_{(in\ sp)} + 2Cu_{(s)} + \tfrac{1}{2}O_{2(g)} = ZnO_{(s)} + Cu_2S_{(s)} \qquad \text{(II)}.$$

The auxiliary system Cu/Cu_2S was used to buffer p (SO_2).
These equilibria are vizualed in a stability diagram for the Zn-Cu-S-O system at 1000 K with logp (SO_2) and logp (O_2) as axes (fig.1).

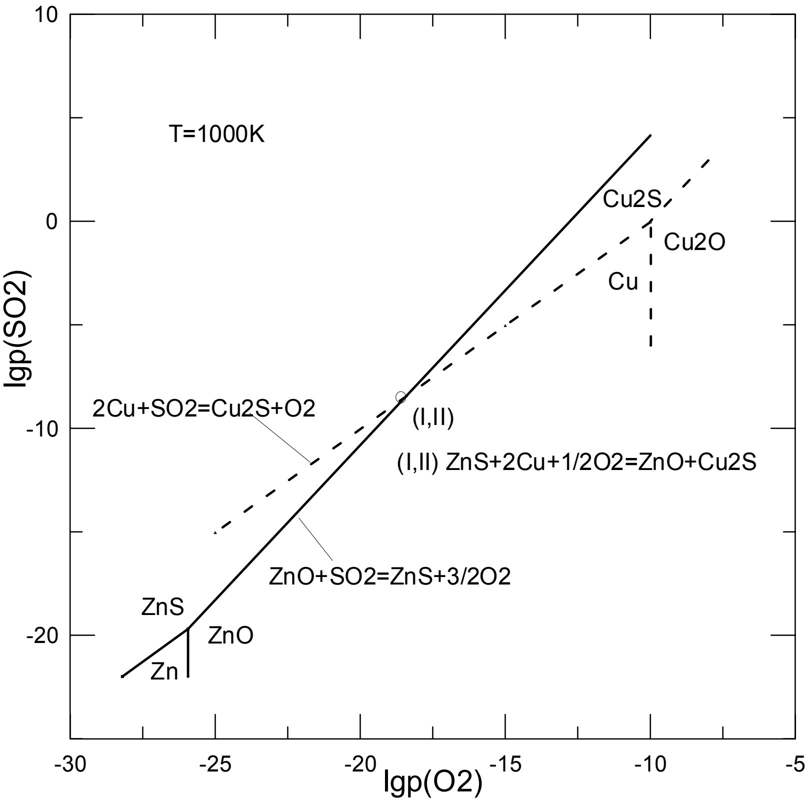

Fig.1. Stability diagram for the Zn-Cu-S-O system at 1000 K.

EXPERIMENTAL

Galvanic cell used. To measure the oxygen pressure in equilibria (I) and (II) the following galvanic cells were prepared:

$$Pt,ZnS,ZnO,Cu_2S,Cu,p(O_2)\ |YSZ|\ NiO,Ni,p^*(O_2),Pt \qquad \text{(A)},$$
$$Pt,ZnS_{(in\ sp)},ZnO,Cu_2S,Cu,p(O_2)\ |YSZ|\ NiO,Ni,p^*(O_2),Pt \qquad \text{(B)},$$

where YSZ are yttria-stabilized zirconium as the solid electrolyte; $p^*(O_2)$ is the oxygen pressure in the reference system.

The sample system was prepared by mixing thoroughly the powder of sphalerite ZnS (sp) or $(Fe_{0,3}Zn_{0,7})S$(ss) solid solution, Cu sulfide Cu_2S, Zn oxide ZnO, metallic Cu in molar ratio of 1:1:1:2 to a total amount of 1,6 g. The mixture was placed in a silica glass tube. The reference system (Ni, NiO) was prepared in a similar manner and placed in a zirconium tube.

Experimental condition

The cells were heated in a vertical resistance furnace 240 mm high with a “uniform” temperature region of 20-25 mm, where the working part of the cell with the sample and reference systems was placed. The cell’s EMF and thermo-EMF were measured with the SCH304-2 digital millivoltmeter with a high input impedance of 10^{12} Ω with the accuracy of ±0,01 mV. To maintain temperature with the accuracy of $\pm0{,}3^{o}$ the thermoregulator PROTERM-100 was used. The thermocouple Pt/Pt (10% mass Rh) was used. The EMF and T values were screened during the experiment. The equilibrium EMF values were obtained by temperature titration, i.e. the equilibrium EMF values were expected at a constant temperature. The equilibrium values were attained at high temperatures in 5-6 hours and at low temperatures in 24 hours on average. The aim of the experiment was thus to get about half of the points at the temperature increase with respect to the previous point, and the others – at the temperature decrease with respect to the previous point. The pairs of points with similar values were obtained at different stages of the experiment in a considerable (sometimes several weeks) period of time.

RESULTS AND CALCULATIONS

EMF values obtained. The EMF values obtained from cells A and B are given in table 1.

Table 1.

T/K, Emeas/mV, and residuals ΔE=Emeas-Ecalc, obtained for cells (A) and (B).

T/K	E(A)meas/ mV	ΔE(A)=E(A)meas-E(A)calc/mV		T/K	E(B)meas/ mV	ΔE (B)=E(B)meas-E(B)calc/mV
848,5	120,67	0,71		834,2	123,45	1,33
848,6	120,71	0,73		865,1	129,64	0,06
868,7	125,63	0,33		875,3	132,07	-0,05
888,4	130,64	0,14		885,2	135,81	-1,00
898,5	133,3	0,15		901,7	139,25	0,37
903,5	134,41	-0,06		917,4	143,625	-0,50
908,7	135,85	0,01		927,5	146,683	-1,09
918,9	138,54	0,01		937,7	149,859	-1,07
923,8	139,72	-0,09		947,9	152,09	-0,95
929,1	141,26	0,05		955,2	152,88	-0,44
939,2	143,9	0,04		961,2	154,81	-0,18
944,1	144,99	-0,16		962,4	155,55	0,20
944,6	144,73	-0,56		970,0	157,41	-0,09
949,7	145,95	-0,66		973,0	158,88	0,53
954,3	147,61	-0,21		980,7	160,79	0,24
959,6	148,52	-0,70		982,5	161,6	0,52
964,2	150,24	-0,18		992,0	164,64	0,80
969,8	151,24	-0,64		1000,1	166,99	0,75
974,5	152,86	-0,25		1001,5	167,01	0,36
979,6	154,17	-0,28		1011,9	170,34	0,60
979,7	154,21	-0,28		1021,1	172,7	0,17
984,3	155,46	-0,23		1032,8	176,3	0,21
989,7	156,88	-0,20		1042,4	179,66	0,59
994,5	158,06	-0,28		1053,1	181,98	-0,45
999,8	159,57	-0,15		1062,4	185,81	0,46
1004,3	160,67	-0,23		1070,8	188,13	0,08
1008,6	162,33	0,31		1082,3	191,3	-0,45
1014,3	163,26	-0,25		1090,1	194,24	-0,07
1019,4	165,05	0,21		1102,0	197,32	-0,93

1024,2	165,79	-0,31
1029,4	167,7	0,25
1034,1	168,33	-0,33
1039,3	170,32	0,30
1044,2	170,9	-0,38
1048,7	172,87	0,42
1054,2	173,62	-0,27
1059,5	175,66	0,40
1069,5	178,31	0,46
1074,6	178,91	-0,27
1079,9	181,03	0,49
1089,5	183,52	0,50
1100,0	186,25	0,50
1109,1	188,85	0,77
1114,9	189,63	0,04
1130,0	194,06	0,59
1154,9	199,76	-0,12
1160,0	201,87	0,69
1220,2	216,58	-0,02
1269,3	228,64	-0,46
1288,8	233,76	-0,29
1308,9	238,86	-0,26

The EMF (E/mV) values obtained are described by the following equations:

$$E\ (A)=(-1{,}31016E\text{-}5)T^2+0{,}287119T-114{,}238 \pm 0{,}32,\ R^2=0{,}9998,\ (849<T/K<1309),$$

$$E\ (B)=0{,}00017972T^2-0{,}0637246T+50{,}2124 \pm 0{,}50,\ R^2=0{,}9991,\ (834<T/K<1102).$$

Calculation of oxygen pressures in equilibria (I) u (II)

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

$$\log p(O_2) = \log p^*(O_2) - (nFE10^{-3})/(R\ln 10T) \qquad (1),$$

where the amount of electrons is n=4 according to the electrode equation $O_2 + 4e^- = 2O^{2-}$; E is the EMF measured/mV; F is the Faraday constant, 96484,56 colomb/mol; R is the gas constant, 8,31441 $J\cdot K^{-1}\cdot mol^{-1}$; T is the absolute temperature/K. Data for the calculation of oxygen pressures in the reference system, according to the equilibrium $Ni_{(s)} + 1/2O_{2(g)} = NiO_{(s)}$, were taken from [1]:

$$\log p^*(O_2) = 8{,}055 - 24274/(T/K) + 0{,}0984*\ln(T/K).$$

The obtained $\log p(O_2)$ values in equilibria (I) и (II) are described by the following equations:

$$\log pO_2(I) = -22{,}3611(1000/T) + 3{,}60371,\ R^2=1,\ (849<T/K<1309),$$

$$\log pO_2(II) = -21{,}997(1000/T) + 3{,}09288,\ R^2=0{,}9998,\ (834<T/K<1102).$$

Calculation of $\Delta_r G^o{}_T(I)$ values

Under the conditions of thermodynamic equilibrium

$$\Delta_r G^o{}_T(I) = -\ln 10RT\cdot\log K \qquad (2),$$

$$\text{where } K(I) = 1/pO_2(I)^{1/2} \qquad (3).$$

Insertion of eqn. (3) into eqn. (2) and a subsequent rearrangement give:

$$\Delta_r G^o{}_T(I) = \tfrac{1}{2}\ln 10RT\cdot\log p(O_2) \qquad (4).$$

$$\Delta_r G^o{}_T(I)=0{,}0691755T-428{,}281\ (kJ\cdot mol^{-1}),\ R^2=0{,}9994,\ (849<T/K<1309).$$

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

According to the equation (I):

$$\Delta_f G^o{}_T(ZnS) = \Delta_f G^o{}_T(ZnO) + \Delta_f G^o{}_T(Cu_2S) - \Delta_r G^o{}_T(I) \qquad (5),$$

where $\Delta_f G^o{}_T(ZnO)$ and $\Delta_f G^o{}_T(Cu_2S)$ values were taken from the thermochemical data [2].

$\Delta_f G^o{}_T(ZnS) = 2{,}21151E\text{-}7T^3 - 0{,}000578658T^2 + 0{,}590369T - 400{,}219\ (kJ\cdot mol^{-1})$,
$R^2=0{,}9997$, $(849<T/K<1309)$.

Calculation of ZnS activities in ($Fe_{0,3}Zn_{0,7}$)S solid solution

As EMF measurements were taken with respect to one reference system in cells A and B, a (ZnS in sp) can be calculated for a “symmetric” cell, where the reference system is the system with pure sphalerite ($a_{ZnS}=1$), and the sample system is the system with sphalerite solid solution ($a_{ZnS}\neq 1$).

As the constants of the equations (I) and (II) can be derived under equilibrium conditions as follows:

$$K\ (I) = 1/pO_2\ (I)^{1/2},\ K\ (II) = 1/[pO_2\ (II)^{1/2}\cdot a\ (ZnS\ in\ sp)],$$

we obtain

$$ZnS\ in\ sp) = [pO_2(I)/pO_2(II)]^{1/2} \qquad (6).$$

On the other hand,

$$E(B)–E(A)= (RT/4F) \cdot \ln[pO_2(I)/pO_2(II)] \qquad (7).$$

Insertion of eqn. (6) into eqn. (7) and a subsequent rearrangement give:

$$\log a\ (ZnS\ в\ sp) = 2F/R \cdot \Delta E/T\quad 10^{-3}/\ln 10,\ где\ \Delta E=E(B)–E(A).$$

The a (ZnS в sp) values are described by the following equation:

a (ZnS in sp) = 5,24775E-6T^2-0,00974623T+5,65769, R^2=0,9996, (849<T/K<1309).

Table 2.

Values of obtained thermodynamical magnitudes at the fixed temperatures

T/K	$\lg pO_2(I)$/atm	$\lg pO_2(II)$/atm	$\Delta_f G^o_T$(ZnS)/ kJ·mol^{-1}	a_{ZnS} in ($Fe_{0,3}Zn_{0,7}$)S	γ_{ZnS}
900	-21,242	-21,348	-176,381	1,137	3,789
1000	-18,757	-18,904	-167,357	1,159	3,864
1100	-16,725	-16,904	-156,637	1,287	4,289
1200	-15,031	-15,238	-142,895	1,519	5,063
1300	-13,597	-13,828	-124,803	1,856	6,188
standard deviation	0,008	0,026	0,180	0,015	0,050

References

1. *Pejrid.L.* (1984). Acta Chem. Scand. A-38. P.242-246.
2. *Barin I.*. (1995). Thermochemical Data of Pure Substances, VCH.