G. P. POPOV, M. I. SIMONOVA, T. A. UGOLNIKOVA,

Corresponding Member of the USSR Academy of Sciences G. I. CHUFAROV

1963

SovietRxiv

Abstract

Full Text

G. P. POPOV, M. I. SIMONOVA, T. A. UGOLNIKOVA,
Corresponding Member of the USSR Academy of Sciences G. I. CHUFAROV

THERMODYNAMIC PROPERTIES AND CRYSTAL-CHEMICAL CHARACTERISTICS OF SOLID SOLUTIONS OF ZINC FERRITE WITH MAGNETITE

In the present work, on the basis of experimentally measured analytical equilibrium constants for the reaction of reduction of $ZnFe_2O_4$ by hydrogen, the principal thermodynamic functions were calculated and the dependence of the parameters of the crystal lattices on the composition of the solid solutions $ZnFe_2O_4$—Fe_3O_4 was determined. The analytical equilibrium constants $K_p = P_{H_2O}/P_{H_2}$ were determined at temperatures of 600, 700, and 900°, as described in (^{1}). The dependences of their values on the composition $Zn_{1-x}Fe_{2+x}O_4$ are given in Fig. 1 and in Table 1. X-ray structural analysis showed that $ZnFe_2O_4$ is reduced to Fe_3O_4, forming a continuous series of solid solutions; moreover, throughout the entire range of compositions the equilibrium product of reduction is the ZnO phase. The compositions of the solid solutions $Zn_{1-x}Fe_{2+x}O_4$ formed in the reduction process were determined from the parameter of the crystal lattices with the aid of the calibration curve presented in Fig. 2. The curve was obtained by measuring the lattice parameter of solid solutions $Zn_{1-x}Fe_{2+x}O_4$ with a prescribed composition. The specimens were prepared by the ceramic method from ZnO and Fe_2O_3 oxides of chemically pure grade and ferrous oxide obtained by reduction of Fe_2O_3 in iron containers at 880° for 40 h. Only those FeO preparations were used which had a parameter of 4.300–4.302 Å.

(Figure: Fig. 1)

Fig. 1

All the investigated specimens of the solid solutions $Zn_{1-x}Fe_{2+x}O_4$ had a cubic lattice of the spinel type. The lattice parameter was calculated from the position of the α_1 peak of the diffraction reflection (444) in chromium radiation. This diffraction reflection was recorded on a URS-50I ionization apparatus by point counting at angular intervals of 5′ with a constant counting time. In finding the angle 2θ, only the correction for displacement of the goniometer zero was taken into account. The course of the change in the lattice parameter $d_{(x)}$, calculated from the obtained values of 2θ, gave a scatter of measurements of no more than 0.001 Å.

Comparison of the parameter values calculated by the indicated method with the values obtained from powder X-ray diffraction patterns of the same specimens shows that the calibration curve may be shifted along the parameter axis by no more than 0.002 Å.

The reproducibility of the results was checked on 5 series of specimens. Analysis of the dependence $d_{(x)}$ by the least-squares method showed that it cannot be represented by a single curve, but is described by two linear sections. The presence of several linear sections is observed in

Table 1

Values of thermodynamic functions of solid solutions $Zn_{1-x}Fe_{2+x}O_4$

x^*	900°C			700°C			600°C			$-\Delta H^0_{298}$, kcal/mole	$-\Delta Z^0_{298}$, kcal/mole		S^0_{298}, cal/deg·mole	Composition of solid solutions
	K_p	P_{O2}, atm	$-\Delta Z$, kcal	K_p	P_{O2}, atm	$-\Delta Z$, kcal	K_p	P_{O2}, atm	$-\Delta Z$, kcal					
0.00	191.00	$1.82 \cdot 10^{-12}$	12.199	95.00	$1.13 \cdot 10^{-17}$	8.805	59.90	$1.79 \cdot 10^{-21}$	7.114	283.5	255.5	1.97	30.78	$ZnFe_2O_4$
0.06	115.00	$6.62 \cdot 10^{-13}$	11.084	42.60	$2.28 \cdot 10^{-18}$	7.248	24.10	$2.91 \cdot 10^{-22}$	5.517	–	–	–	–	–
0.12	85.90	$3.69 \cdot 10^{-13}$	10.363	33.10	$1.37 \cdot 10^{-18}$	6.762	18.00	$1.61 \cdot 10^{-22}$	5.014	–	–	–	–	–
0.22	47.90	$1.40 \cdot 10^{-13}$	8.875	20.20	$5.51 \cdot 10^{-19}$	5.981	12.20	$7.45 \cdot 10^{-23}$	4.502	–	–	–	–	–
0.27	24.50	$2.29 \cdot 10^{-14}$	7.498	11.70	$1.72 \cdot 10^{-19}$	4.757	7.70	$2.25 \cdot 10^{-23}$	3.544	275.5	250.0	7.5	30.40	$Zn_{0.7}Fe_{2.3}O_4$
0.38	18.70	$1.75 \cdot 10^{-14}$	6.709	8.90	$9.92 \cdot 10^{-20}$	4.232	5.20	$1.35 \cdot 10^{-23}$	2.793	–	–	–	–	–
0.52	11.10	$6.17 \cdot 10^{-15}$	5.517	4.95	$3.06 \cdot 10^{-20}$	3.094	3.18	$5.13 \cdot 10^{-24}$	0.960	273.8	246.0	5.5	33.0	$Zn_{0.5}Fe_{2.5}O_4$
0.63	5.00	$1.25 \cdot 10^{-15}$	3.753	2.20	$6.08 \cdot 10^{-21}$	1.357	0.95	$4.06 \cdot 10^{-25}$	−0.087	–	–	–	–	–
0.72	4.00	$8.01 \cdot 10^{-16}$	3.237	1.89	$4.49 \cdot 10^{-21}$	1.230	0.94	$4.00 \cdot 10^{-25}$	−0.164	269.3	244.0	2.53	33.3	$Zn_{0.3}Fe_{2.7}O_4$
0.83	3.70	$6.91 \cdot 10^{-16}$	3.049	1.80	$4.07 \cdot 10^{-21}$	1.133	0.90	$4.00 \cdot 10^{-25}$	−0.183	–	–	–	–	–
0.92	3.20	$5.13 \cdot 10^{-16}$	2.697	1.55	$3.01 \cdot 10^{-21}$	0.848	0.90	$4.00 \cdot 10^{-25}$	−0.183	266.6	240.0	6.53	34.00	$Zn_{0.1}Fe_{2.9}O_4$
1.00	–	–	–	–	–	–	–	–	–	270.0**	242.0**	–	35.00**	Fe_3O_4

* x is the mole fraction of Fe_3O_4 in $Zn_{1-x}Fe_{2+x}O_4$.

** Literature data.

in the system $FeCr_2O_4 - Fe_3O_4$, which likewise represents solid solutions of the normal and inverse structures (^{2}). The change of the parameter in solid solutions

$Zn_{1-x}Fe_{2+x}O_4$ was studied in work (^{3}), but its authors could not distinguish two linear portions on the $d_{(x)}$ curve. Knowledge of the compositions of the solid solutions made it possible to write the equations of the chemical reactions for the reduction of ferrite by hydrogen in the following form:

$$Zn_2FeO_4 + yH_2 = cZnO + Zn_{1-c}Fe_2O_{4-c-y} + yH_2O,$$

where c is the mole fraction of Fe_3O_4 in the solid solutions $Zn_{1-c}Fe_2O_{4-c-y}$. From the experimentally found values of the analytical equilibrium constants (Fig. 1), the principal thermodynamic properties of solid solutions of zinc ferrite with magnetite were calculated (Table 1). The values of C_p for $ZnFe_2O_4$ were taken from the data of work (^{4}), and for the other substances from work (^{5}).

The dissociation elasticities of the solid solutions P_{O2} were calculated by the formula

$$P_{\mathrm{O2}}^{1/2} = K_{\mathrm{H2O}} \cdot K_p,$$

where K_{H2O} is the dissociation constant of water vapor. The variation of P_{O2} with composition and temperature is conveyed by the following equations:

a) for stoichiometric ferrite, as a function of temperature,

$$\lg P_{\mathrm{O2}\,\mathrm{ZnFe_2O_4}} = 14.80 - 3.074 \cdot 10^3/T;$$

b) for solid solutions $Zn_{1-x}F_{2+x}O_4$, as a function of composition,

$$\lg P_{\mathrm{O2}\,900^\circ\mathrm{C}} = -11.74 - 6.06 \cdot x + 2.76 \cdot x^2,$$

$$\lg P_{\mathrm{O2}\,700^\circ\mathrm{C}} = -16.866 - 7.98 \cdot x + 4.30 \cdot x^2,$$

$$\lg P_{\mathrm{O2}\,600^\circ\mathrm{C}} = -20.745 - 7.53 \cdot x + 3.31 \cdot x^2.$$

The values of the dissociation elasticities as functions of temperature and composition can be expressed by the surface equation:

$$\lg P_{\mathrm{O2}\,T_i,x_i} = 14.455 - 30.7 \cdot 10^3 \cdot T^{-1} + 34.22 \cdot x - 81.40 \cdot 10^3 \cdot T^{-1} \cdot x +$$

$$+39.10 \cdot 10^6 \cdot T^{-2} \cdot x - 68.05 \cdot x^2 + 144.80 \cdot 10^3 \cdot T^{-1} \cdot x^2 - 72.40 \cdot 10^6 \cdot T^{-2} \cdot x^2.$$

The isobaric-isothermal potentials of the reduction reaction of $Zn_{1-x}Fe_{2+x}O_4$ by hydrogen, as functions of temperature and composition, are described by the following equations:

as a function of temperature

$$\Delta F^0_{\mathrm{ZnFe2O_4}} = 7604 - 6.5 \cdot T \lg T + 1.5 \cdot 10^{-3} \cdot T^2 - 7.784 \cdot 10^5 \cdot T^{-1} + 1.973 \cdot T,$$

$$\Delta F^0_{\mathrm{Zn_{0.7}Fe_{2.3}O_4}} = 8566 - 2.042 \cdot T \lg T + 0.451 \cdot 10^{-3} \cdot T^2 - 5.86 \cdot 10^5 \cdot T^{-1} - 7.5 \cdot T,$$

$$\Delta F^0_{\mathrm{Zn_{0.5}Fe_{2.5}O_4}} = 7833 - 5.64 \cdot T \lg T + 0.734 \cdot 10^{-3} \cdot T^2 - 6.444 \cdot 10^5 T^{-1} + 5.5 \cdot T,$$

$$\Delta F^0_{\mathrm{Zn_{0.3}Fe_{2.7}O_4}} = 9735 - 4.63 \cdot T \lg T + 1.04 \cdot 10^{-3} \cdot T^2 - 7.02 \cdot 10^5 \cdot T^{-1} + 2.53 \cdot T,$$

$$\Delta F^0_{\mathrm{Zn_{0.1}Fe_{2.9}O_4}} = 8949 - 5.67 \cdot T \lg T + 1.35 \cdot 10^{-3} \cdot T^2 - 7.417 \cdot 10^5 \cdot T^{-1} + 6.53 \cdot T;$$

as a function of composition

$$\Delta F^0_{900^\circ\mathrm{C}} = -12.234 + 18.395 \cdot x - 8.505 \cdot x^2,$$

$$\Delta F^0_{700^\circ\mathrm{C}} = -8.746 + 16.623 \cdot x - 8.746 \cdot x^2,$$

$$\Delta F^0_{600^\circ\mathrm{C}} = -7.06 + 15.406 \cdot x - 8.187 \cdot x^2.$$

The values of ΔF^0 as functions of temperature and composition are

$$\Delta F^0_{T_i, x_i} = -27.284 + 17.65 \cdot 10^3 \cdot T^{-1} + 26.865 \cdot x - 10.02 \cdot 10^3 \cdot T^{-1} \cdot x +$$

$$+ 38.02 \cdot 10^6 \cdot T^{-1} \cdot x^2 - 72.99 \cdot 10^3 \cdot T^{-1} \cdot x^2 + 25.98 \cdot x^2.$$

The dependences of the standard enthalpy and isobaric-isothermal potential of formation of ferrites from the elements, ΔH^0_{298} and ΔZ^0_{298}, although close to linear, are more accurately represented by the equations:

$$-\Delta H^0_{298\,\mathrm{Zn}_{1-x}\mathrm{Fe}_{2+x}\mathrm{O}_4} = \exp\left(1.0673 - 1.305 \cdot 10^{-2} \cdot x\right),$$

$$-\Delta Z^0_{298\,\mathrm{Zn}_{1-x}\mathrm{Fe}_{2+x}\mathrm{O}_4} = \exp\left(1.0477 - 1.183 \cdot 10^{-2} \cdot x\right).$$

The value of ΔH^0_{298} for $ZnFe_2O_4$ was obtained as −283.5 kcal/mol, which is close to the value −284.0 kcal/mol calculated from the data of works ([6],[7],[8]), and to the value −286.5 kcal/mol given in work ([9]).

For measuring the standard entropies of the reduction reaction of solid solutions, the following equations are proposed:

$$\Delta S^0_{\mathrm{ZnFe2O}_4} = 0.857 + 6.5\lg T - 3.005 \cdot 10^{-3} \cdot T - 7.784 \cdot 10^5 \cdot T^{-2},$$

$$\Delta S^0_{\mathrm{Zn}_{0.7}\mathrm{Fe}_{2.3}\mathrm{O}_4} = 8.388 + 2.042\lg T - 0.902 \cdot 10^{-3} \cdot T - 5.86 \cdot 10^5 \cdot T^{-2},$$

$$\Delta S^0_{\mathrm{Zn}_{0.5}\mathrm{Fe}_{2.5}\mathrm{O}_4} = -3.043 + 5.64\lg T - 1.474 \cdot 10^{-3} \cdot T - 6.444 \cdot 10^5 \cdot T^{-2},$$

$$\Delta S^0_{\mathrm{Zn}_{0.3}\mathrm{Fe}_{2.7}\mathrm{O}_4} = -0.526 + 4.63\lg T - 2.098 \cdot 10^{-3} \cdot T - 7.02 \cdot 10^5 \cdot T^{-2},$$

$$\Delta S^0_{\mathrm{Zn}_{0.1}\mathrm{Fe}_{2.9}\mathrm{O}_4} = -4.05 + 5.67\lg T - 2.705 \cdot 10^{-3} \cdot T - 7.417 \cdot 10^5 \cdot T^{-2}.$$

By Hess' s law, the standard entropies of formation of ferrites from the elements were calculated; their values are given in Table 1. The value of S^0_{298} for $ZnFe_2O_4$ was obtained as somewhat smaller than that estimated by approximate calculation methods in work ([10]). The dependence of the standard entropies on the composition of $Zn_{1-x}Fe_{2+x}O_4$ is shown in Fig. 3. From this figure it is seen that, when the concentration of Fe^{2+} ions in the solid solutions changes from 0 to 0.3, the entropy value, within the error of measurement and calculation, ±0.7 e.u., remains constant; with a further increase in concentration it rises markedly from 30.78 e.u. to 35.00 e.u.

It is necessary to note the fact that the intersection of the straight-line dependences $S_{(x)}$ occurs at the same concentration as for $a_{(x)}$, Figs. 2 and 3. This

is connected with the peculiarities of the formation of solid solutions in the system $ZnFe_2O_4$ and Fe_3O_4.

Zinc ferrite is a normal spinel, whereas magnetite is an inverse spinel ([11,12]), whose structures may be written as $Zn^{2+}[Fe^{3+}]O_4$ and $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$, where the square brackets contain the cations occupying octahedral sites, and before the brackets are the ions occupying tetrahedral sites. From the standpoint of the distribution of cations over the sublattices, zinc ferrite is a more ordered system, since Zn^{2+} ions occupy only tetrahedral sites, and Fe^{3+} ions octahedral sites.

(Figure: Fig. 2)

Fig. 2

Therefore the entropy of $ZnFe_2O_4$ must have a smaller value than that for Fe_3O_4, which is confirmed by comparison of the obtained entropy value of $ZnFe_2O_4$, 30.78 e.u., with the entropy value of Fe_3O_4, 35.00 e.u.

The process of formation of solid solutions between $ZnFe_2O_4$ and Fe_3O_4 reduces to the replacement of Zn^{2+} ions by Fe^{2+} ions and to a redistribution of cations over the tetrahedral and octahedral positions. Since the curves $S(x)$ and $a(x)$ each have two qualitatively different sections, it may be assumed that the degree of inversion changes differently in these sections. The constancy of the entropy or, possibly, its very slow increase in the first section indicates that in the concentration interval $0 \leq x \leq 0.3$ no noticeable disordering occurs in the distribution of cations over the sublattices, i.e., the degree of inversion practically does not change. The slight change in the crystal-lattice parameter in this section can be explained by the substitution of Zn^{2+} ions by Fe^{2+} ions, close to them in size, in tetrahedral sites, which also indicates the constancy of the degree of inversion or its insignificant change, since the slope of this section is small.

(Figure: Fig. 3)

Fig. 3

In the second section, from $x = 0.3$ to $x = 1.0$, a more rapid decrease in the parameter and increase in entropy are observed than in the first section. Such a change in the course of the dependences $a(x)$ and $S(x)$ is connected with a strong change in the degree of inversion as a function of composition.

Institute of Metallurgy
Ural Branch of the Academy of Sciences of the USSR

Institute of Metal Physics
Academy of Sciences of the USSR

Received
14 VII 1962

REFERENCES CITED

1. G. P. Popov, DAN, **140**, No. 6, 1338 (1961).

2. H. J. Jearian, J. M. Kortright, R. H. Langenheim, J. Chem. Phys., **22**, 7, 1196 (1954).

3. N. Migata, J. Phys. Soc. Japan, **16**, 7, 1296 (1961).

4. L. Bokhirol, C. R., **232**, 1474 (1951).

5. O. Kubaschewski, E. Evans, *Thermochemistry in Metallurgy*, IL, 1954, p. 318.

6. A. N. Krestovnikov, T. G. Toropova, *Physics and Physicochemical Analysis*, **1**, No. 3, Moscow, 1957, p. 362.

7. V. I. Smirnov, *Reflecting Smelting*, Moscow, 1952, p. 66.

8. V. D. Mishin, Tr. Ural Industrial Institute, **21**, 9 (1945).

9. L. A. Reznitskii, *Thermodynamic Investigation of Ferrites*, author' s abstract of dissertation, Moscow State University, 1960.

10. A. I. Okunev, N. P. Diev, Tr. Inst. Metallurgii UFAN, **1**, 71 (1957).

11. H. Schmalzried, Zs. phys. Chem. (neue Folge), **31**, 184 (1962).

12. J. M. Hastings; L. M. Corliss, Revs. Mod. Phys., **25**, 114 (1953).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.