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G. P. Popov and Corresponding Member of the Academy of  
Sciences of the USSR G. I. Chufarov

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**Abstract****Full Text**

# ACTIVITIES, HEATS, AND ENTROPIES OF MIXING IN SOLID SOLUTIONS

# NiFe<sub>2</sub>O<sub>4</sub>—Fe<sub>3</sub>O<sub>4</sub>

**G. P. Popov and Corresponding Member of the Academy of Sciences of the USSR G. I. Chufarov**

*Chemistry*

The equilibrium conditions of solid solutions NiFe<sub>2</sub>O<sub>4</sub>—Fe<sub>3</sub>O<sub>4</sub> during the reduction of nickel ferrite by hydrogen were investigated under equilibrium conditions at various temperatures. A weighed portion of NiFe<sub>2</sub>O<sub>4</sub> was placed in a closed vacuum apparatus in which a mixture of H<sub>2</sub> + H<sub>2</sub>O circulated. The water-vapor pressure corresponded to the saturated vapor pressure at 0°C. Equilibrium was attained both from the reduction side and from the oxidation side, and the average hydrogen-pressure values were taken as equilibrium values  $P_{\text{H}_2}$ . These data are given in Table 1. From the values of the equilibrium hydrogen pressures, the equilibrium constants of the reduction reaction were calculated:

$$K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$$

(Figure: Fig. 1. Change in the activities of ferrite and magnetite in the NiFe<sub>2</sub>O<sub>4</sub>—Fe<sub>3</sub>O<sub>4</sub> system as a function of composition: 1 —900°; 2 —800°; 3 —700°; 4 —600°)

**Fig. 1.** Change in the activities of ferrite and magnetite in the NiFe<sub>2</sub>O<sub>4</sub>—Fe<sub>3</sub>O<sub>4</sub> system as a function of composition: 1 —900°; 2 —800°; 3 —700°; 4 —600°

X-ray structural analysis of the reaction products showed that, upon reduction of NiFe<sub>2</sub>O<sub>4</sub>, metallic Ni with an admixture of Fe and the solid solution NiFe<sub>2</sub>O<sub>4</sub>—Fe<sub>3</sub>O<sub>4</sub> are formed. On the basis of the change in the lattice parameter of the metallic phase and the data of work (1), the mole fractions of NiFe<sub>2</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> in the solid solutions were calculated (Table 1). Knowledge of the mole fraction of ferrite  $N_\phi$  and magnetite  $N_m$  and of the equilibrium constants made it possible to calculate the activities of ferrite  $a_\phi$  and magnetite  $a_m$  in solid solutions of variable composition. Ferrite reduced by 0.1% was taken as the standard state. The activity of ferrite was determined as

$$a_\phi = \frac{K_{p_i}}{K_{p_0}},$$

and the activity coefficient—from the equation

$$a_\phi = \gamma_\phi N_\phi.$$

The activities of Fe<sub>3</sub>O<sub>4</sub> were calculated by graphical integration of the Gibbs-Duhem equation:

$$\ln a_\phi = - \int \frac{1 - N_\phi}{N_\phi} d \ln a_m.$$

**Table 1**

**Activities of the components of solid solutions of the system NiFe<sub>2</sub>O<sub>4</sub>—Fe<sub>3</sub>O<sub>4</sub>**

$N_\phi$ 900° 800° 700° 600°C																			
$P_{H_2} a_\phi$				$a_M \gamma_\phi$				$\gamma_M$				$P_{H_2} a_\phi$							
mm				mm				mm				mm							
Hg				Hg				Hg				Hg							
0.160	0.031	1.000	0.000	0.000	0.000	0.000	0.041	1.000	0.000	0.000	0.000	0.046	0.000	0.000	0.000	0.048	0.000	0.000	0.000
0.850	0.036	0.903	0.007	0.056	0.050	0.046	0.892	0.006	0.042	0.040	0.052	0.883	0.002	0.030	0.017	0.058	0.816	0.000	0.952
0.717	0.040	0.770	0.090	0.078	0.316	0.054	0.764	0.082	0.068	0.290	0.064	0.720	0.053	0.993	0.187	0.080	0.597	0.026	0.835
0.436	0.057	0.530	0.373	0.220	0.660	0.080	0.505	0.360	0.160	0.638	0.109	0.420	0.309	0.965	0.547	0.140	0.305	0.240	0.700
0.179	0.107	0.280	0.665	0.570	0.810	0.142	0.289	0.665	0.620	0.810	0.190	0.240	0.636	0.345	0.775	0.320	0.150	0.613	0.839
0.020	0.189	0.159	0.953	0.940	0.970	0.295	0.138	0.953	0.900	0.970	0.440	0.103	0.945	0.150	0.965	0.610	0.078	0.937	0.910

The activity coefficient of Fe<sub>3</sub>O<sub>4</sub> was determined as

$$\gamma_M = \frac{a_M}{1 - N_\phi}.$$

These data are given in Table 1. The change in activities is shown in Fig. 1.

The partial free energies of mixing were calculated by the formula  $\Delta \bar{F}_i = RT \ln a_i$ , and the total free energy of mixing from the expression

$$\Delta F_{pi} = \Delta \bar{F}_{\phi_i} \cdot N_{\phi_i} + \Delta \bar{F}_{Mi} \cdot N_{Mi}.$$

Since the temperature dependence of these functions is very weak, their values were averaged, and these data are presented in Fig. 2.

Applying the theory of regular solutions (2) to solid solutions of ferrites, we find the partial enthalpy of mixing from the formula:

$$4.575 \lg \gamma_i = \Delta \bar{H}_i \frac{1}{T} + \text{const},$$

and the total enthalpies of mixing from the expression

$$\Delta H_{pi} = \Delta \bar{H}_{\phi_i} \cdot N_{\phi_i} + \Delta \bar{H}_{Mi} \cdot N_{Mi}.$$

The partial entropies were calculated similarly to how this was done in work <sup>(3)</sup>, from the expression

$$\Delta \bar{S}_i = \frac{\Delta \bar{H}_i - \Delta \bar{F}_i}{T},$$

and the total entropy was calculated by the formula

$$\Delta S_{pi} = \Delta \bar{S}_{\phi_i} \cdot N_{\phi_i} + \Delta \bar{S}_{Mi} \cdot N_{Mi}.$$

Since the dependence of the entropies on temperature is very weak, averaged values were calculated and are presented in Fig. 3.

The excess entropies of mixing were calculated similarly to how this was done in work <sup>(4)</sup>, from the expression

$$\Delta S_{i \text{ excess}} = \Delta \bar{S}_i - \Delta S_{i \text{ ideal}}.$$

From the theory of regular solutions it follows <sup>(5)</sup> that  $\Delta S_{i \text{ ideal}} = -R \ln N_i$ . Excess entropies of mixing usually have a complex dependence on composi-

value. For the compositions studied at 900°C, this dependence is represented by the curves shown in Fig. 3. The excess entropies characterize the degree of ordering of the solid solutions. As a first approximation one may

(Figure: Fig. 2)

**Fig. 2.** Change in the partial free energies and enthalpies of mixing in solid solutions of the system  $\text{NiFe}_2\text{O}_4\text{—Fe}_3\text{O}_4$ :

1— $\Delta \bar{H}_{\phi}$ , 2— $\Delta \bar{F}_{\phi}$ , 3— $\Delta \bar{F}_n$ , 4— $\Delta H_n$ , 5— $\Delta \bar{F}_M$ , 6— $\Delta \bar{H}_M$ .

(Figure: Fig. 3)

**Fig. 3.** Change in the entropies of mixing in solid solutions of the system  $\text{NiFe}_2\text{O}_4\text{—Fe}_3\text{O}_4$  as a function of composition:

1— $\Delta S_{\phi}$ , 2— $\Delta S_{\phi \text{ excess}}$ , 3— $\Delta S_n$ , 4— $\Delta S_{n \text{ excess}}$ , 5— $\Delta S_M$ , 6— $\Delta S_{M \text{ excess}}$ .

assume that the degree of ordering in the  $\text{NiFe}_2\text{O}_4\text{—Fe}_3\text{O}_4$  system changes for  $\text{NiFe}_2\text{O}_4$  according to curve 2, for  $\text{Fe}_3\text{O}_4$  according to curve 6, and, overall, for the solid solution according to curve 4.

Institute of Metallurgy

Ural Branch of the Academy of Sciences of the USSR

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## REFERENCES

1. A. E. Bradly, A. H. Jay, A. Taylor, *Phil. Mag.*, **23**, 545 (1937).
2. G. Hildebrand, *Solubility of Nonelectrolytes*, Moscow, 1938.
3. K. Sanbongi, *Sci. Rep.*, **1**, 213 (1949).
4. A. V. Shashkina, Ya. I. Gerasimov, *ZhFKh*, **27**, 399 (1953).
5. O. Kubaschewski, A. Schneider, *Zs. Elektrochem.*, **49**, 261 (1943).

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

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