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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

Chemistry

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On the Equilibrium Conditions in the Reduction of Nickel Ferrite by Hydrogen

(Presented by Academician G. V. Kurdyumov, May 20, 1961)

In works ([1]-[3]) it has been shown that the mechanism of reduction of nickel ferrite depends substantially on the ratio of the rates of the chemical reaction and diffusion in the solid phase. In the present work, the equilibrium conditions during the reduction of nickel ferrite were determined, i.e., the compositions and nature of the gaseous and solid phases.

The reduction was carried out with hydrogen in a closed vacuum apparatus with circulation of an $H_2 + H_2O$ mixture by means of a mercury pump. The water-vapor pressure

Fig. 1. Change in the equilibrium constant during the reduction of nickel ferrite by hydrogen as a function of the degree of reduction at temperatures: 1 –900°, 2 –800°, 3 –700°, 4 –600°

Fig. 2. Change in the parameters of the crystal lattices of the phases: 1 –spinel, 2 –wüstite, 3 –metallic –during the reduction of nickel ferrite by hydrogen

was maintained equal to the pressure of saturated vapor at 0°C. After equilibrium had been established, the ferrite sample was removed from the furnace by an electromagnetic device, the water vapor was frozen out in a trap immersed in liquid nitrogen, and the hydrogen pressure was measured. The attainment of equilibrium was effected both from the reduction side and from the oxidation side, and the average value of the hydrogen pressures was taken as the equilibrium value.

value. The degree of reduction was determined from the consumption of hydrogen. The nature of the solid phases coexisting with the gas phase was determined by X-ray diffraction, by the Debye method, in a chamber 57.3 mm in diameter.

The photographs were taken in Fe–K_α radiation using a Mn filter. To determine the parameters of the crystal lattices, graphical extrapolation according to Bradley and Jay was used.

Nickel ferrite was obtained by sintering an equimolar mixture of NiO and Fe_2O_3 at 1200° for 30 h in air and had a crystal-lattice parameter of 8.332 ± 0.005 Å, in agreement with the data of [3]. Figure 1 and Table 1 give experimentally determined equilibrium constants

$$K_p = \frac{P_{H_2O}}{P_{H_2}}$$

at different temperatures and degrees of reduction. Figure 2 presents the results of X-ray phase analysis of the reduction products and the changes in the parameters of their crystal lattices.

Reduction of $NiFe_2O_4$ proceeds in two stages. From 0 to 60% reduction, the reaction product is a metallic phase, initially consisting of almost pure nickel. As the degree of reduction increases, iron accumulates in it and the crystal-lattice parameter grows to 3.56 Å at 60%. At the same time the lattice parameter of the ferrite increases from 8.332 to 8.378 Å, i.e., to a value corresponding to almost pure magnetite (Fig. 2). Thus, in the first stage of reduction, nickel ferrite is gradually enriched in iron, forming a series of solid solutions from $NiFe_2O_4$ to Fe_3O_4. Accordingly, as the process proceeds, the equilibrium constant changes, and its value at 60% reduction approaches the value corresponding to the equilibrium Fe_3O_4–FeO (Fig. 1).

The second stage of reduction is characterized by the appearance of wüstite with a lattice parameter of 4.28 Å and continues from 60 to 100%. Here reduction of wüstite to iron takes place; therefore the lattice parameter of the metallic phase increases to 3.584 Å at 75%. Subsequently, after 75% reduction, it apparently changes,

Table 1

Thermodynamic quantities of the $NiFe_2O_4$–Fe_3O_4 system

No.	Degree of reduction, %	900°C K_p	900°C P_{O_2}, atm	900°C $-\Delta Z$, kcal	800°C K_p	800°C P_{O_2}, atm	800°C $-\Delta Z$, kcal	700°C K_p	700°C P_{O_2}, atm	700°C $-\Delta Z$, kcal	600°C K_p	600°C P_{O_2}, atm	600°C $-\Delta Z$, kcal	$-Q_{298}$, kcal/mol H_2O	$-\Delta H_{298}$, kcal/mol	$-\Delta F_{298}$, kcal/mol	S_{298}, cal/deg·mol	Composition of solid ferrite solutions
1	0.1	151.1	$0.14 \cdot 10^{-12}$	11.69	111.4	$0.97 \cdot 10^{-14}$	10.09	99.8	$0.25 \cdot 10^{-17}$	8.65	95.7	$0.60 \cdot 10^{-21}$	7.91	—	257.0	236.6 —	47.0	$NiFe_2O_4$

No.	Degree of reduction, %	900°C K_p	900°C P_{O_2}, atm	900°C $-\Delta Z$, kcal	800°C K_p	800°C P_{O_2}, atm	800°C $-\Delta Z$, kcal	700°C K_p	700°C P_{O_2}, atm	700°C $-\Delta Z$, kcal	600°C K_p	600°C P_{O_2}, atm	600°C $-\Delta Z$, kcal	$-Q_{298}$, kcal/mol H_2O	$-\Delta H_{298}$, kcal/mol	ΔF_{298}, kcal/mol		S_{298}, cal/deg·mol	Composition of solid ferrite solutions
2	5	136.50	—	11.49	99.31	—	9.80	88.10	—	8.42	78.11	—	7.55	—	—	—	—	—	—
3	10	111.6	$5.40 \cdot 10^{-13}$	11.08	95.12	$2.88 \cdot 10^{-15}$	9.47	71.06	$6.35 \cdot 10^{-18}$	8.02	57.20	$1.60 \cdot 10^{-21}$	7.01	7.47	257.0	235.5	48.80	47.0	$Ni_{0.727}Fe_{2.260}O_4$
4	20	80.16	$3.20 \cdot 10^{-13}$	10.21	56.31	$1.20 \cdot 10^{-15}$	8.60	44.11	$2.07 \cdot 10^{-18}$	7.03	29.14	$4.20 \cdot 10^{-22}$	5.58	—	—	—	—	—	—
5	30	42.70	$1.20 \cdot 10^{-13}$	8.74	32.23	$4.12 \cdot 10^{-16}$	7.40	24.17	$4.34 \cdot 10^{-19}$	5.97	14.30	$1.04 \cdot 10^{-22}$	4.58	2.57	263.5	239.2	36.35	40.4	$Ni_{0.258}Fe_{2.742}O_4$
6	40	24.12	$2.85 \cdot 10^{-14}$	7.41	15.59	$2.74 \cdot 10^{-17}$	5.84	10.30	$1.25 \cdot 10^{-19}$	4.35	7.50	$1.80 \cdot 10^{-23}$	3.14	1.86	—	—	37.006	—	—
7	45	15.08	$1.12 \cdot 10^{-14}$	6.27	10.44	$1.30 \cdot 10^{-17}$	4.10	7.22	$6.55 \cdot 10^{-20}$	3.71	3.98	$7.95 \cdot 10^{-24}$	2.44	15.20*	266.5*	242.5*	18.98*	35.00*	Fe_3O_4
8	50	9.80	$4.84 \cdot 10^{-15}$	5.31	6.40	$4.00 \cdot 10^{-18}$	3.95	4.30	$2.40 \cdot 10^{-20}$	2.74	0.16	$1.53 \cdot 10^{-26}$	0.92	—	—	—	—	—	—
9	60	3.00	—	—	1.80	—	—	0.98	—	—	0.15	—	—	—	—	—	—	—	—
10	75	0.91	$4.85 \cdot 10^{-17}$	—	0.72	$2.06 \cdot 10^{-19}$	—	0.43	$2.40 \cdot 10^{-22}$	—	0.08	$3.36 \cdot 10^{-27}$	—	—	—	—	—	—	—

according to work (4); however, within the limits of accuracy of our measurements, these changes are not detected.

On the basis of the values obtained for the lattice parameters of the metallic phase and from the data of work (4), the composition of the ferrite as a function of the degree of reduction was calculated (Table 1).

Knowledge of the equilibrium constants for the reduction by hydrogen of the solid solutions $NiFe_2O_4$–Fe_3O_4 made it possible to calculate for them the change in the oxygen dissociation elasticity P_{O2} and in the isobaric-isothermal potential of the reduction reaction ΔZ. The changes in the standard heat of the reduction reaction Q_{298}, as well as the standard free energies ΔF°_{298} and the standard enthalpies ΔH_{298} of formation from the elements of $NiFe_2O_4$ and of the solid solutions, were calculated. The value of ΔH_{298} for $NiFe_2O_4$ was determined to be 257.0 kcal/mole and is close to that indicated (258 kcal/mole) in work (5).

All these data are given in Table 1, which also indicates the values of the integration constants I in the equation of the reaction isobar and the standard values of the absolute entropies of the ferrite solid solutions S_{298}, calculated with the aid of the Temkin–Schwarzman equation (6).

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