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Abstract

Full Text

Chemistry

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EQUILIBRIUM CONDITIONS IN THE SYSTEMS Co–O AND Co–O–H

The existence of two cobalt oxides has been reliably established: CoO and Co_3O_4, of which the first has a crystal lattice of the NaCl type, and the second, of the spinel type ([1]). X-ray structural studies carried out by us on samples of Co_2O_3 from the Krasnyi Khimik plant showed that this preparation has a spinel-type crystal lattice with a parameter close to the parameters of Co_3O_4.

However, determining the value of the parameter with sufficient accuracy proved very difficult because of the broadening of the lines on the X-ray pattern. Reports should be noted that anhydrous Co_2O_3 cannot be individualized ([2]), and that CoO and Co_3O_4 are capable of forming solid solutions with oxygen ([3]).

In works devoted to determining the dissociation elasticities of cobalt oxides and the equilibrium in the Co–O–H system ([4–11]), data are given that differ considerably from one another, which has led to the necessity of undertaking new investigations. These questions are of considerable interest for the production of cobalt and its compounds, especially for the technology of direct production of high-quality metallic cobalt from its oxides by reduction of the latter with hydrogen.

Cobaltous-cobaltic oxide. Cobaltous-cobaltic oxide was prepared by calcining "cobalt oxide" of chemically pure analytical grade at 800° C for 70 hours in an atmosphere of air. X-ray structural studies of the preparation obtained showed that it is single-phase and has a spinel structure with a lattice parameter coinciding with literature data ([1]). Its oxygen content proved to be close to the stoichiometric content in Co_3O_4. The equilibrium oxygen pressures were determined in a vacuum apparatus ([12]). Temperature measurement was carried out directly above the specimen under investigation, and its fluctuations amounted to no more than $±$1°. Measurement of pressures in the range 10^{-5}–10 mm Hg was carried out with a set of MacLeod manometers.

Table 1

Equilibrium oxygen pressure in the system
$Co_3O_4 \rightleftarrows 3CoO + \frac{1}{2}O_2$

T, °K	923	973	1073	1123	1173
P_{O_2}, mm	$5.32 \cdot 10^{-2}$	0.12	7.3	25.0	153.5

The equilibrium $Co_3O_4 \rightleftarrows 3CoO + \frac{1}{2}O_2$ was studied both from the side of dissociation of Co_3O_4 and from the side of oxidation of CoO. The average values of the equilibrium oxygen pressures obtained in this way are given in Table 1. They are described by the equation:

$$\lg P_{O_2} = -\frac{16522}{T} + 13.4,$$

where P_{O2} is in atmospheres, and the change in isobaric-isothermal potential is

$$\Delta Z_T^0 = 37794 - 30.652\,T \text{ cal.}$$

Owing to the high dissociation pressure of Co_3O_4, direct study of the equilibrium

$$Co_3O_4 + H_2 \rightleftarrows 3CoO + H_2O$$

is difficult because of the low equilibrium pressure of hydrogen. But from the equilibrium conditions in this system of two interrelated processes:

$$Co_3O_4 \rightleftarrows 3CoO + \tfrac{1}{2}O_2$$

and the dissociation of water vapor

$$H_2O \rightleftarrows H_2 + \tfrac{1}{2}O_2,$$

for which [13]

$$\lg K_{H2O} = -\frac{13160}{T} + 3.05,$$

expressions have been found for the temperature dependence of the equilibrium constant

$$\lg K' = \lg \frac{P_{H2O}}{P_{H2}} = \frac{4899}{T} + 3.65$$

and of the change in isobaric-isothermal potential

$$\Delta Z_T^0 = -22413 - 16.699\,T \text{ cal.}$$

The exothermic character of the reaction, $\Delta H^0_{298.1} = -19412$ cal, causes the equilibrium constant to decrease with increasing temperature.

Cobaltous oxide. In studies of the equilibrium [6–9]

$$CoO + H_2 \rightleftarrows Co + H_2O$$

methods with substantial shortcomings were used. Thus, in particular, in work [9] thermal diffusion was not taken into account and the equilibrium gas mixture was not analyzed.

For the investigation, cobaltous oxide of chemically pure grade was used. X-ray structural analysis established that it was single-phase and that the lattice parameter corresponded to the literature data [1]. The study was carried out in the same vacuum apparatus. To eliminate the influence of thermal diffusion, continuous circulation of the gas mixture was carried out by a diffusion pump. Equilibrium was reached at a constant water-vapor pressure equal to 4.579 mm, which was maintained by immersing a trap with water in a Dewar vessel with melting ice. When equilibrium was attained, the sample was removed from the furnace, quenched, and the vapor-gas mixture was separated by freezing out the water vapor in a trap immersed in liquid nitrogen. The equilibrium gas was analyzed for foreign impurities by interaction of hydrogen with cobaltous oxide, which for this purpose was again introduced into the heating furnace, while the resulting H_2O vapor was frozen out. The pressure difference was equal to the equilibrium pressure of hydrogen, which, with the aid of a correction graph, was recalculated to the actual hydrogen pressure in the equilibrium state, when the trap had a temperature of 0°. The equilibrium of the reaction was studied both from the reduction side and from the oxidation side.

From the experimental data obtained, presented in Table 2 and described by the relation

$$\lg K'' = \frac{973.4}{T} + 0.52,$$

it follows that with increasing temperature the equilibrium constant decreases. This is explained by the exothermic character of the process, $\Delta H^0_{298.1} = -631$ cal. [9]. The change in isobaric-isothermal potential is determined by the equation

$$\Delta Z^0_T = -4457 - 2.381\,T \text{ cal.}$$

Table 2

Equilibrium constants of the process $CoO + H_2 \rightleftarrows Co + H_2O$

T, °K	$P_{H2}^{equil.}$, mm Hg	$K'' = \frac{4.579}{P_{H2}}$	Conditions	K'' average
773	0.0821	55.77	From the reduction side	56.32
773	0.0805	56.88	From the oxidation side	56.32
873	0.0975	46.96	From the reduction side	46.60
873	0.0990	46.25	From the oxidation side	46.60
973	0.1303	35.14	From the reduction side	35.10
973	0.1306	35.06	From the oxidation side	35.10
1073	0.1801	25.43	From the reduction side	25.86
1073	0.1742	26.29	From the oxidation side	25.86
1173	0.2155	21.25	From the reduction side	21.07
1173	0.2192	20.89	From the oxidation side	21.07

The dissociation pressure of cobaltous oxide can be calculated on the basis of

$$P_{O2} = (K_{H2O} K'')^2 \text{ atm.},$$

whence

$$\lg P_{O2} = -\frac{24373}{T} + 7.14,$$

and the change in the isobaric-isothermal potential is

$$\Delta Z_T^0 = 55754 - 16.333\,T \text{ cal.}$$

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