MECHANISM OF THE DECOMPOSITION OF COBALTOUS COMPOUNDS IN VACUO

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ABSTRACT

The decomposition of cobaltous compounds (nitrate, hydroxide, carbonate, oxalate and oxyhydroxide) in vacuo has been investigated by magnetic methods and thermogravimetry. The mechanism is shown to be similar to that in air and begins with the formation of Co^{3+} ions in octahedral coordination The formation of different final products (Co_3O_4, CoO and Co) has been attributed to the nature of the initial cobaltous compound. The results are in agreement with thermodynamic calculations.

INTRODUCTION

It is known that thermal decomposition of cobaltous salts in air leads to the formation of Co_3O_4 [1], whereas decomposition in vacuo produces various products, depending on the nature of the initial cobaltous compound. Thus, as a result of cobaltous oxalate decomposition in vacuo or in an inert medium, metallic Co and CoO are obtained [2—7], whereas the decomposition product of cobaltous carbonate or hydroxide is CoO [8—11]. and that of CoOOH in an inert medium is Co_3O_4 [12]. From a thermodynamic point of view, identical conditions of decomposition should lead to the same products. The differences observed may be due to differences in the conditions arising during the decomposition of cobaltous compounds in vacuo. For this reason, the decomposition of different cobaltous compounds in vacuo was studied by measuring their magnetic properties during thermal treatment. This method was chosen because the magnetic methods are highly sensitive to the presence of small amounts of ferromagnetic admixtures, such as ferromagnetic cobalt, and give information on the valency state of the transition metal and its environment.

EXPERIMENTAL

Commercially available $CoC_2O_4 \cdot 4 H_2O$, $Co(NO_3)_2 \cdot 6 H_2O$ (AR, Merck), $2 CoCO_3 \cdot 3 Co(OH)_2 \cdot n H_2O$ (AR, Carlo Erba) and CoOOH (chemically pure, Soyuzkhimeksport) were used. $Co(OH)_2$ was obtained by precipitation

of $Co(NO_3)_2$ with NaOH in the absence of air. The method and apparatus are described in detail in ref. 1. The investigations were carried out in the temperature range 25—370°C and a vacuum of more than 10^{-5} torr. Changes in weight and magnetic properties of the sample were traced simultaneously during the decomposition process.

RESULTS

Figure 1 shows results from measurements of the magnetic susceptibility of $Co(NO_3)_2 \cdot 6 H_2O$ (curve 1) and the decrease in weight of the sample (curve 2) during its decomposition in vacuo. It is evident that, during evacuation of the sample, the gram-atom magnetic susceptibility of the Co ion has already begun to decrease at 25°C due to partial dehydration. The sample weight decreases monotonically at temperatures up to 200°C while the magnetic susceptibility shows complex changes. At 200°C $\mathcal{K}_a$ sharply decreases and the decomposition is practically complete.

Figure 2 presents results from measurements of the temperature dependence of the magnetic susceptibility at some intermediate stages of the decomposition of $Co(NO_3)_2 \cdot 6 H_2O$ obtained by quenching the process (curves 1—10), and also the temperature dependence of the final product of decomposition in vacuo (curve 11). Obviously, the Curie—Weiss law is observed. The respective magnetic moments and Weiss constants are given in Table 1. The similar values of the magnetic moments of the Co ion in the decomposition products up to 140°C (curves 1—4) show that, in this range, only the water of crystallization is eliminated and no change in the valency state of the Co ion occurs. When the sample is heated at a higher temperature, the magnetic moment decreases, passes through a minimum (2.35 BM) and then increases to 2.6 BM. The results of the magnetic studies show that the final decomposition product of $Co(NO_3)_2 \cdot 6 H_2O$ in vacuo is Co_3O_4, the
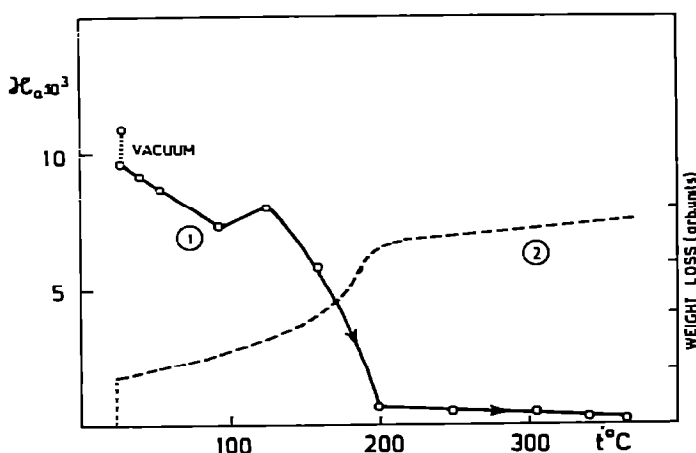

Fig. 1. Change of the gram-atom magnetic susceptibility, $\mathcal{K}_a$, (curve 1) and decrease in weight (curve 2) of a $Co(NO_3)_2 \cdot 6 H_2O$ sample during decomposition in vacuo.
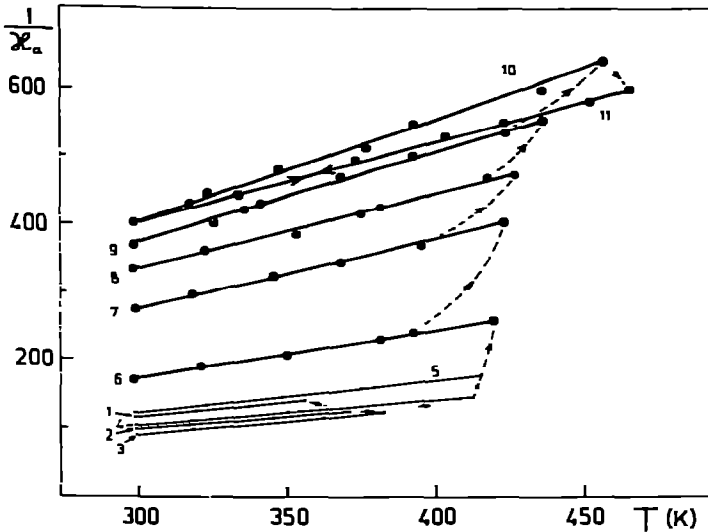
Fig. 2. Dependence of $1/\mathcal{H}_a$ on temperature for different decomposition stages of $Co(NO_3)_2 \cdot 6\ H_2O$

mechanism of the process being the same as that in air [1], i.e. the first decomposition stage is the formation of Co^{3+} ions in octahedral coordination.

It should be noted that the mean magnetic moment of the Co ion in Co_3O_4 increases on heating in vacuo at $350°C$. Table 2 contains the magnetic moments and Weiss constants for different heating durations. The increase in the mean magnetic moment of the Co ion is due to the reduction $Co^{3+}_{octa} \rightarrow Co^{2+}_{octa}$. After heat treatment in vacuo at $350°C$ for 6 h, Co_3O_4 is almost completely reduced to CoO. No similar effect was observed with thermal treatment in vacuo, at the same temperatures, of Co_3O_4 obtained as a result of $Co(NO_3)_2 \cdot 6\ H_2O$ decomposition in air.

Figure 3 shows the changes in magnetic susceptibility, $\mathcal{H}_a$, (curve 1) and decrease in weight (curve 2) of a $Co(OH)_2$ sample during its decomposition in vacuo. At $120—140°C$, both $\mathcal{H}_a$ and the sample weight decrease sharply due to the formation of CoO in vacuo. Figure 4 shows data on the temperature dependence of the magnetic susceptibility of the initial $Co(OH)_2$ (curve

TABLE 1

Changes in the effective magnetic moment of the Co ion (μ_{eff}) and Weiss constant (θ) at different stages of $Co(NO_3)_2 \cdot 6H_2O$ decomposition in vacuo

μ_{eff} (BM)	θ (K)	μ_{eff} (BM)	θ (K)	μ_{eff} (BM)	θ (K)
4.59	−11	4.27	+17	2.42	+23
4.45	+58	3.33	+62	2.35	+20
4.67	+43	2.91	+14	2.64	−57
4.63	+21	2.70	−6		

TABLE 2

Changes in the effective magnetic moment (μ_{eff}) of the Co ion and Weiss constant (θ) of Co_3O_4 during heat treatment at 350°C in vacuo (The sample was obtained by thermal decomposition of $Co(NO_3)_2 \cdot 6H_2O$ at 200°C in vacuo)

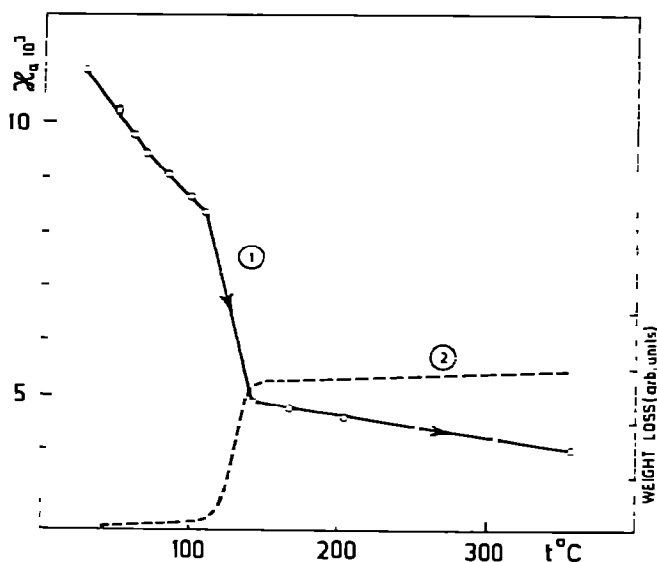| Heating duration (h)	μ_{eff} (BM)	θ (K)
1.5	2 89	−157
4.5	4.12	−193
6.0	5.49	−436

Fig. 3. Change in the gram-atom magnetic susceptibility, $\mathcal{K}_a$, (curve 1) and decrease in weight (curve 2) of $Co(OH)_2$ durings its decomposition in vacuo.
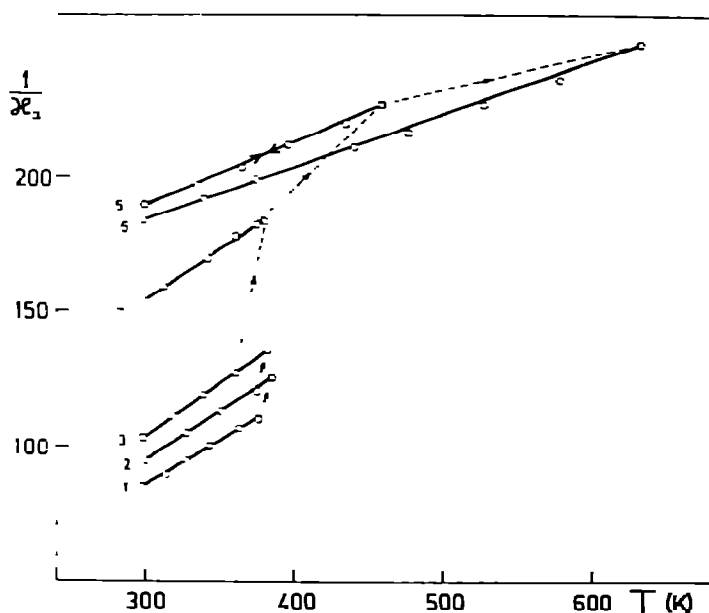

Fig. 4. Dependence of $1/\mathcal{K}_a$ on temperature for different decomposition stages of $Co(OH)_2$.

TABLE 3

Changes in the effective magnetic moment (μ_{eff}) of the Co ion and Weiss constant (θ) at different stages of $Co(OH)_2$ decomposition in vacuo

μ_{eff} (BM)	θ (K)	μ_{eff} (BM)	θ (K)
4.95	+36	4.62	−114
4.88	+14	5.74	−483
4.60	+5	6.44	−658

1), the final product CoO (curve 5), and some intermediate stages of the decomposition of $Co(OH)_2$ (curves 2—4). The corresponding effective magnetic moments, μ_{eff}, and Weiss constants of the Co ion are given in Table 3. The magnetic moment of $Co(OH)_2$ is in good agreement with the results of Richardson and Vernon [13]. The magnetic moment of the Co ion in CoO is higher than those obtained with samples prepared at 1100°C in air. A similar effect was observed by Bielanski et al. [9] with CoO samples obtained from basic cobaltous carbonate in vacuo. During the process of decomposition, the magnetic moment of the Co ion decreases from 4.95 BM (Co^{2+} in a distorted octahedron) to a minimum of 4.6 BM and then increases up to 5.75 BM (Co^{2+} in octahedral coordination). The magnetic moment of the obtained CoO increases with increasing temperature up to 350°C and reaches a value of 6.4 BM (curve 6 in Fig. 4). The presence of a ferromagnetic component has been established. This means that the process continues and leads to the formation of metallic cobalt.
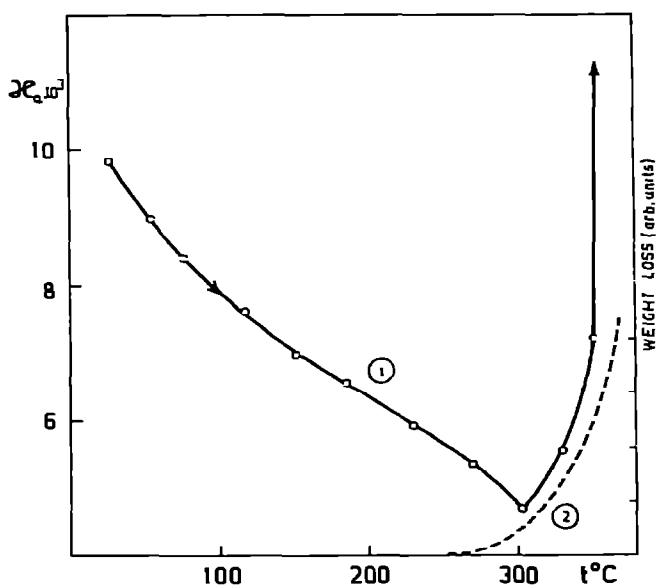

Fig. 5. Change in the gram-atom magnetic susceptibility, χ_d, (curve 1) and decrease in weight (curve 2) of $2\ CoCO_3\ 3\ Co(OH)_2\ n\ H_2O$ during decomposition in vacuo.
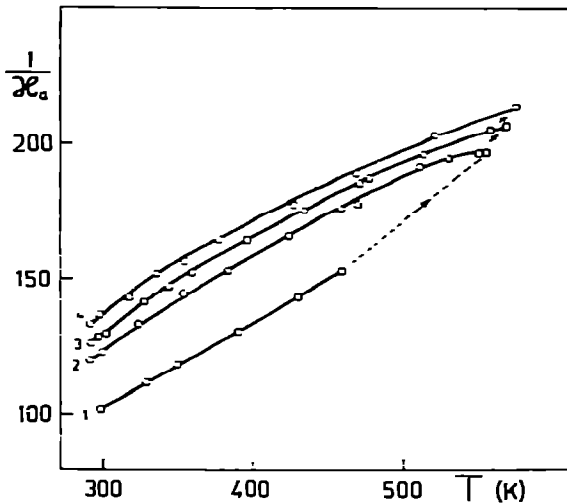
Fig. 6. Dependence of $1/\mathcal{H}_a$ on temperature at some intermediate stages of 2 $CoCO_3$ · 3 $Co(OH)_2$ · H_2O decomposition.

Figure 5 shows results from investigations on the magnetic susceptibility, $\mathcal{H}_a$, of 2 $CoCO_3$ · 3 $CO(OH)_2$ · n H_2O (curve 1) and the decrease in weight of the sample during its decomposition in vacuo. Intensive decomposition of the salts begins at temperatures above 300°C. $\mathcal{H}_a$ strongly increases and a ferromagnetic component is established, i.e. the decomposition proceeds with the formation of metallic cobalt. Figure 6 shows results from studies of the thermal dependence of the initial 2 $CoCO_3$ · 3 $Co(OH)_2$ · n H_2O (curve 1) and some intermediate stages of the decomposition process (dependences
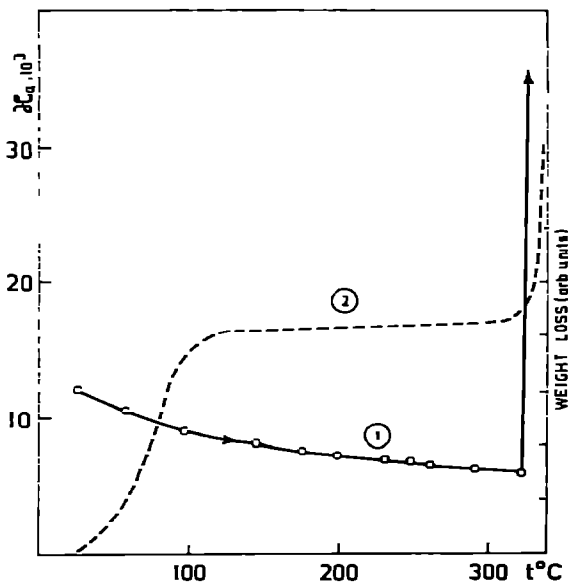

Fig. 7. Change in the gram-atom magnetic suceptibility, $\mathcal{H}_a$, (curve 1) and decrease in weight (curve 2) of CoC_2O_4 · 4 H_2O during decomposition in vacuo

2—4). With the initial sample, the Curie—Weiss law is observed, the effective magnetic moment being 5.0 BM and the Weiss constant $\theta = -22$ K. The intermediate stages of the decomposition process show deviations from the Curie—Weiss law. The experimentally determined values for the effective magnetic moment of the Co ion at 290—360 K (where the $1/\mathfrak{K}_a$ vs. T dependence is linear) vary between 4.4 and 4.2 BM, i.e. values lower than those characteristic of Co^{2+}_{octa} are obtained.

Figure 7 shows the changes in magnetic susceptibility (curve 1) and weight (curve 2) of a $CoC_2O_4 \cdot 4 H_2O$ sample during its decomposition in vacuo. Up to 100°C, the decrease in weight of the sample is due to the removal of its water of crystallization. The effective magnetic moment of the Co ion in CoC_2O_4 was found to be 5.63 BM, and the Weiss constant was $\theta = -68$ K. Above 320°C, the weight of the sample sharply decreases and the sample becomes ferromagnetic due to the formation of ferromagnetic cobalt. The presence of a ferromagnetic component was also established during the intermediate stages of CoC_2O_4 decomposition.

Figure 8 presents the changes in magnetic susceptibility, $\mathfrak{K}_a$, (curve 1) and decrease in weight (curve 3) of a CoOOH sample during its decomposition in vacuo. Intensive decomposition of the sample begins above 220—230°C. Curve 2 corresponds to the magnetic susceptibility of the final product of CoOOH decomposition in vacuo, Co_3O_4. The effective magnetic moment of the Co ion in Co_3O_4 and Weiss constant, as calculated in the temperature range 130—300 K, are 2.76 BM and —82 K, respectively. The Co_3O_4 obtained is stable over the whole temperature range investigated (up to 350°C).
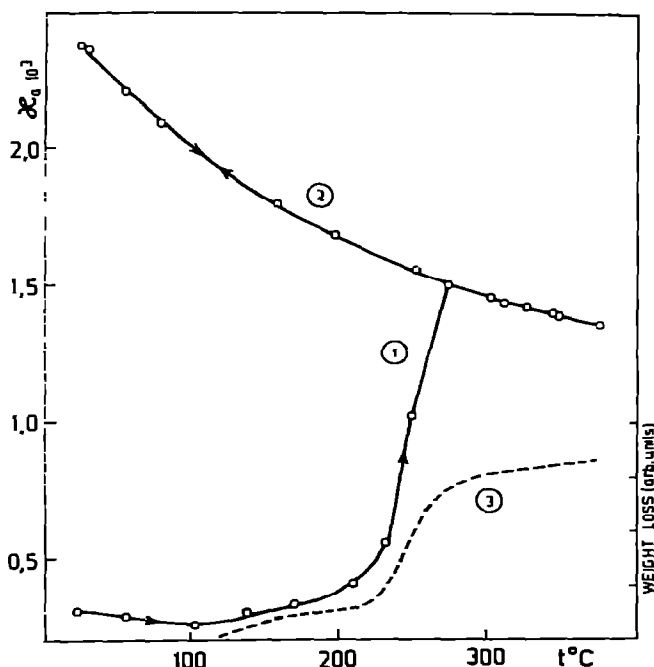

Fig 8. Dependence of the gram-atom magnetic susceptibility, $\mathfrak{K}_a$, and the change in weight of CoOOH on the temperature. 1, Magnetic susceptibility of the initial sample; 2, magnetic susceptibility of the final product; 3, decrease in weight of the sample.

DISCUSSION

The magnetic measurements during the process of decomposition of cobaltous salts in vacuo confirmed the formation of various final products, Co_3O_4, CoO and Co, depending on the nature of the initial cobaltous salt. However, a thermodynamic study of the reaction

$$Co + \frac{x}{2} O_2 \rightarrow CoO_x$$
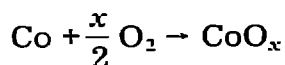
showed $CoO_{1.33}$ (Co_3O_4) to be the stable phase in the temperature range investigated (Fig. 9). The change in the Gibbs free energy ΔG_T depending on temperature at $x = 1$; 1.33; 1.5 and an oxygen pressure of 10^{-6} torr was determined according to ref. 14. A stable Co_3O_4 phase in the cases under consideration was obtained only with decomposition of $Co(NO_3)_2 \cdot 6 H_2O$ and CoOOH in vacuo. The strongest contradiction between our results and the thermodynamic data was observed with $Co(OH)_2$, which has a low decomposition temperature.

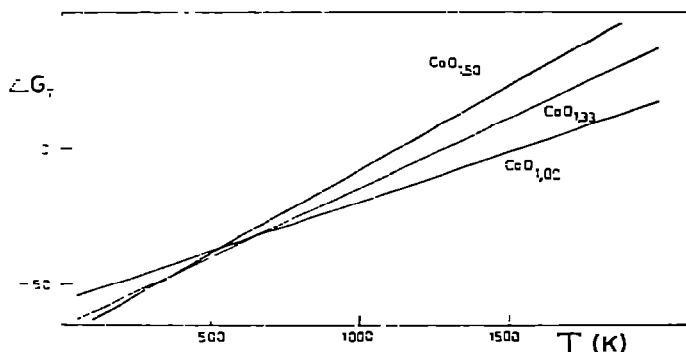The following chemical reactions lead to the formation of Co_3O_4 or CoO depending on the initial compound

$$3 Co(NO_3)_2 \rightarrow Co_3O_4 + 6 NO_2 + O_2 \tag{1}$$

$$2 Co(NO_3)_2 \rightarrow 2 CoO + 4 NO_2 + O_2 \tag{2}$$

$$3 Co(OH)_2 \rightarrow Co_3O_4 + H_2 + 2 H_2O \tag{3}$$

$$Co(OH)_2 \rightarrow CoO + H_2O \tag{4}$$

$$3 CoCO_3 \rightarrow Co_3O_4 + CO + 2 CO_2 \tag{5}$$

$$CoCO_3 \rightarrow CoO + CO_2 \tag{6}$$

$$3 CoC_2O_4 \rightarrow Co_3O_4 + 4 CO + 2 CO_2 \tag{7}$$

$$CoC_2O_4 \rightarrow CoO + CO + CO_2 \tag{8}$$

$$12 CoOOH \rightarrow 4 Co_3O_4 + 6 H_2O + O_2 \tag{9}$$

$$4 CoOOH \rightarrow 4 CoO + 2 H_2O + O_2 \tag{10}$$

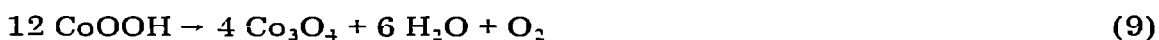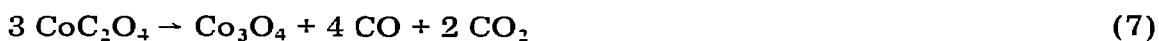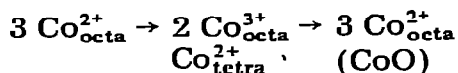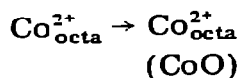
Fig. 9. Dependence of the Gibbs free energy, ΔG_T on temperature for a CoO_x sample ($x = 1$; 1.33; 1.5; oxygen pressure = 10^{-6} torr).

The formation of Co_3O_4 as a stable phase in the decomposition of $Co(NO_3)_2 \cdot 6\,H_2O$ and $CoOOH$ shows that the process takes place according to reactions (1) and (9). When $Co(OH)_2$, $2\,CoCO_3 \cdot 3\,Co(OH)_2 \cdot n\,H_2O$ and $CoC_2O_4 \cdot 4\,H_2O$ are decomposed, the formation of Co_3O_4 is accompanied by the evolution of some reducing gases such as H_2 and CO (reactions 3, 5 and 7), whereas the decomposition of $CoC_2O_4 \cdot 4\,H_2O$ leads to the evolution of CO even when CoO is obtained (reaction 8). However, the ferromagnetic component in the decomposition product is observed with the last three compounds. In this case, the formation of CoO occurs according to the possible mechanisms

$$3\,Co^{2+}_{octa} \rightarrow 2\,Co^{3+}_{octa} \rightarrow 3\,Co^{2+}_{octa}$$
$$Co^{2+}_{tetra} \quad (CoO)$$

or

$$Co^{2+}_{octa} \rightarrow Co^{2+}_{octa}$$
$$(CoO)$$

We are of the opinion that the decomposition of cobaltous salts proceeds according to the first mechanism, which is in agreement with the thermodynamic data, since the experiments showed a minimum in the magnetic moment during the decomposition process. This indicates the presence of Co^{3+}_{octa} ions with a magnetic moment $\mu_{eff}(Co^{3+}_{octa}) = 0$ at the intermediate stages of the decomposition process. With decomposition of $Co(OH)_2$, $2\,CoCO_3 \cdot 3\,Co(OH)_2 \cdot n\,H_2O$ and $CoC_2O_4 \cdot 4\,H_2O$, the Co^{3+} ions formed are accompanied by a reducing gas (H_2, CO, respectively) which leads to CoO as a final product and even to metallic Co. No reducing gas is evolved with decomposition of $CoOOH$ and $Co(NO_3)_2 \cdot 6\,H_2O$, due to which Co_3O_4 is stabilized. This opinion is confirmed by the fact that, according to our experimental results, no ferromagnetic component is obtained during decomposition of $2\,CoCO_3 \cdot 3\,CO(OH)_2 \cdot n\,H_2O$ in the presence of another easily reducible oxide (CuO). This means that CoO and Co are obtained as a result of the reducing action of the evolved CO and H_2.

The stable phase above $400°C$ in vacuo is CoO. For this reason, the Co_3O_4 obtained at lower temperatures is reduced to CoO under these conditions. However, it should be taken into account that this process also depends on the stoichiometry of the initial Co_3O_4 and its defect structure. That is why the Co_3O_4 obtained from $CoOOH$ in vacuo or from $Co(NO_3) \cdot 6\,H_2O$ in air is not reduced at a noticeable rate at $350°C$, whereas Co_3O_4 obtained from $Co(NO_3) \cdot 6\,H_2O$ in vacuo gradually passes into CoO.

On the basis of the present study it may be concluded that the decomposition mechanism of cobaltous compounds in vacuo is similar to that in air, i.e. the process begins with the formation of Co^{3+} ions in octahedral coordination. However, the Co_3O_4 phase is not always stabilized; this depends on the nature of the initial cobaltous salt.

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