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THERMAL INVESTIGATION OF THE BASIC COPPER(II) NITRATE $Cu(OH)_{1.5}(NO_3)_{0.5}$

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A thermal investigation of basic copper(II) nitrate was made under dynamic heating conditions as well as in an isothermal environment. Data analysis was applied to calculate the heat of thermal decomposition of gerhardtite (21.6$\pm$0.1 kcal/mole), which does not depend on the heating rate from 4°/min to 20°/min.

Basic copper(II) nitrate, $Cu(OH)_{1.5}(NO_3)_{0.5}$, known in nature as gerhardtite, has been used by one of the present authors [1] to study the complex formations of copper(II) ions with methylamine and diethylamine. It is known that the usual method for determining the stability constants with such ligands (CH_3NH_2, $(C_2H_5)_2NH$) cannot be used because of the fact that they completely precipitate copper(II) ions in the pH range the amine complexes are formed in.

There are no data available in the literature on the thermal behaviour of basic copper(II) nitrate. The aim of this paper is to supply some information on the thermal decomposition of gerhardtite, and to calculate the heat of decomposition at various rates of heating.

Experimental

Synthetic gerhardtite was prepared according to [1] and the crystals were washed and dried at 80°. $Cu(OH)_{1.5}(NO_3)_{0.5}$ was analyzed for copper by electrolysis and the copper content were found to be 53.1% (theoretical values 53.0%).

Thermoanalytical studies were carried out with a derivatograph [2] in air atmosphere. Samples of 151.8 mg, 157.2 mg, 448.0 mh and 170.8 mg were weighed into a platinum crucible. The rate of heating was 20°/min, 15°/min, 8°/min or 4°/min. Thermogravimetry in an isothermal environment were made with a Q-derivatograph [3]. A sample of 170 mg was weighed into a labyrinth crucible and the TG curve in an isothermal environment was obtained.

Results and discussion

The thermoanalytical curve $Cu(OH)_{1.5}(NO_3)_{0.5}$ is presented in Fig. 1. As reflected by the thermal curve, the decomposition begins at about 205°. The endothermic effect at 290° can be assigned to the reaction:

$$3\,Cu(OH)_2.Cu(NO_3)_2 = 4\,CuO + 3\,H_2O + 2\,NO_2 + 1/2\,O_2 + \Delta H \qquad (1)$$

The theoretical weight loss (according to reaction (1)) is 33.75% and the calculated one (according to Figs 1. and 2) is 33.6%.

In Fig. 2, TG curves of $Cu(OH)_{1.5}(NO_3)_{0.5}$ are compared in an isothermal environment (curve 1) and under dynamic heating conditions (curve 2). We can arrive at the conclusion that the mechanism of thermal decomposition of gerhardtite

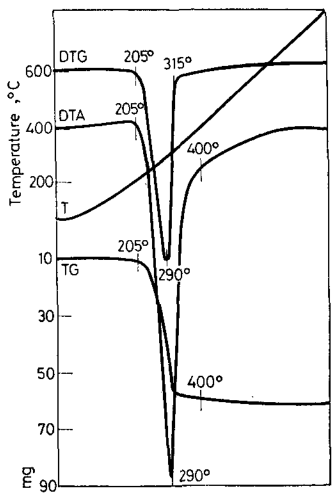

Fig. 1. Thermoanalytical curves of $Cu(OH)_{1.5}(NO_3)_{0.5}$

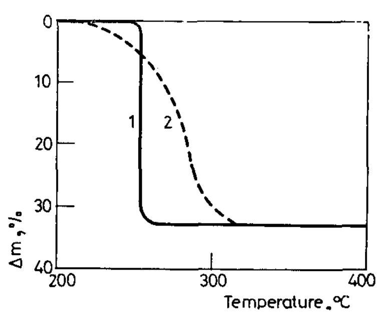

Fig. 2. TG curves of $Cu(OH)_{1.5}(NO_3)_{0.5}$. 1 — in an isothermal environment; 2 — under dynamic heating conditions

proceeded to a degree according to reaction (1). This was confirmed by X-ray diffraction data for the samples at 340° and 800°, which show that in both cases CuO (monoclinic tenorite) is obtained.

The heat of decomposition of gerhardtite was obtained by analyzing the TG curves [4] of $Cu(OH)_{1.5}(NO_3)_{0.5}$ at various rates of heating. Figure 3 shows the dependence of the percentage weight loss (log Δm) as a function of temperature in Kelvin. It is obvious that the heat of decomposition remains practically the same (21.6 ± 0.1 kcal/mole) from 4°/min to 20°/min, which is an indication that the real process is in equilibrium.

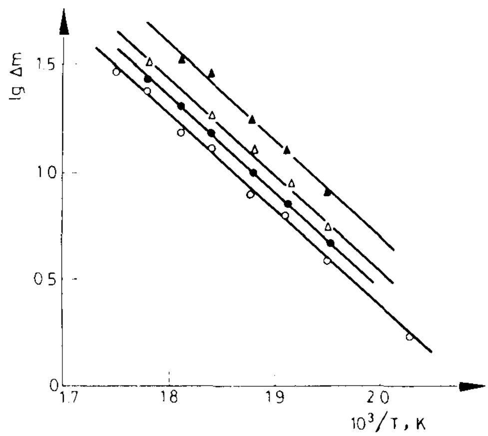

Fig. 3. log Δm as a function of $1/T$ at various rates of heating in °/min: ▲ 4; △ 8; • 15; ○ 20

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