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Abstract

Full Text

CHEMISTRY

A. N. KHLAPOVA

PHASE TRANSFORMATIONS IN THE SODIUM SULFATE–SODIUM CARBONATE SYSTEM

(Presented by Academician I. I. Chernyaev, 31 XII 1957)

In contrast to (1-5), the present study of melts of sulfate with sodium carbonate was carried out on the same samples simultaneously by differential-thermographic, X-ray, and crystal-optical methods of phase analysis. The melts were examined 1-5 days after their preparation, and also after storage for about 1-2 months without access of atmospheric moisture and for more than a year openly in air under laboratory conditions.

The results obtained are presented in Figs. 1 and 2.

From the phase diagram of the system $\text{Na}_2\text{SO}_4\text{--Na}_2\text{CO}_3$ (Fig. 1) it is seen that the high-temperature solid solution sodium sulfate–sodium carbonate, crystallizing from a melt of the salts, undergoes a series of phase transitions on cooling. The process of phase transformations with temperature in this system is governed primarily by the presence of polymorphism in sodium sulfate and sodium carbonate (6-10). Thus, the continuous series of δ -solid solutions formed between the high-temperature δ -modifications of the initial components ($\delta\text{-Na}_2\text{SO}_4$ (6, 7) and $\delta\text{-Na}_2\text{CO}_3$ (8)) near 600° (the temperature of the $\delta\gamma$ polymorphic transformations of the pure salts) over the entire concentration range is transformed into an unlimited γ -solid solution, which forms between $\gamma\text{-Na}_2\text{SO}_4$ (6, 7, 9) and $\gamma\text{-Na}_2\text{CO}_3$ (8, 10).

The γ -solid solution, depending on the composition of the melt, decomposes at different temperatures along a complex curve. In the middle part of the diagram, on this curve near 400° there are two maxima, one of which lies at 66.3 mol.% Na_2SO_4 and corresponds to the formation in the solid state of a double salt of composition $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ (hexagonal burkeite (11)), while the other—at 25.0 mol.% Na_2SO_4 —corresponds to the formation of a double salt of composition $\text{Na}_2\text{SO}_4 \cdot 3\text{Na}_2\text{CO}_3$. Between these chemical compounds, on the basis of hexagonal burkeite (11), a phase of variable composition (γ' -phase) is formed, extending at ordinary temperatures within the limits of ~13.0 to 75.0 mol.% Na_2CO_3 .

On the basis of the β -modification of sodium sulfate (6), as shown in Fig. 1, a limited β -solid solution is formed, from which, at approximately 130° , a third chemical compound of sodium sulfate with sodium carbonate, of composition

$9\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ (ϵ -phase), separates. This double salt practically does not form solid solutions with its constituent components.

The α' - and β' -phases, located in the region rich in Na_2CO_3 (Fig. 1), are limited solid solutions of sodium sulfate, respectively, in the α - and β -modifications of sodium carbonate (^{8, 10}).

The X-ray and crystal-optical characteristics of the low-temperature solid phases of the Na_2SO_4 – Na_2CO_3 system are given in (¹¹).

The present study established that the α -, β -, ϵ -, γ' - and α' -solid phases, as well as the double salts of compositions $9\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$, $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ and $\text{Na}_2\text{SO}_4 \cdot 3\text{Na}_2\text{CO}_3$ (Fig. 1), which are stable without access of moisture, at ap- in the absence of water vapor, or under atmospheric conditions, become unstable, metastable, as a result of the fact that H_2O vapors, chemically interacting with the two-component sodium sulfate–carbonate melts, behave in this case as a third component of the system. Therefore all

Fig. 1. Phase-equilibrium diagram of melts of the system Na_2SO_4 – Na_2CO_3 that were not subjected to the action of moisture after melting of the salts. Data of differential thermal analysis (from heating curves of two samples): **1** –liquidus, **2** –solidus. Data of X-ray diffraction analysis: **3** –single-phase, **4** –two-phase; the γ' -phase, formed on the basis of the compounds $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$ and $\text{Na}_2\text{SO}_4 \cdot 3\text{Na}_2\text{CO}_3$, extends from 13.0 to 75.0 mole % Na_2CO_3 .

low-temperature solid phases of the binary system Na_2SO_4 – Na_2CO_3 (Fig. 1), tending toward equilibrium with H_2O , gradually, as moisture penetrates into the depth of the crystals, are transformed (depending on the composition of the melt), as shown in Fig. 2, into thenardite (T -phase), rhombic burkeite (γ'' -phase), and soda monohydrate (x -phase), which usually form from super-saturated aqueous solutions of the ternary system Na_2SO_4 – Na_2CO_3 – H_2O (^{2, 6, 11, 12}).

In works (^{6, 11}) it was reported that thenardite and rhombic burkeite contain in their crystals an insignificant amount (fractions of wt. %) of structurally bound water.

As a result of the present investigation, new data have been obtained on phase transformations in the system Na_2SO_4 – Na_2CO_3 , and a fundamental difference has been revealed in the nature of the solid phases formed between sodium sulfate and sodium carbonate in the melt and in aqueous solutions of these salts.

Fig. 2. Phase-equilibrium diagram of melts of the Na_2SO_4 – Na_2CO_3 system in the presence of water vapor and under atmospheric conditions: T –phase with the structure of thenardite, γ'' –phase with the structure of rhombic burkeite, χ –phase with the structure of soda monohydrate.

It has been established that sodium sulfate–carbonate melts in the presence of water vapor and under atmospheric conditions undergo a transformation from a

Fig. 2. Phase-equilibrium diagram of melts of the $\text{Na}_2\text{SO}_4\text{--Na}_2\text{CO}_3$ system in the presence of water vapor and under atmospheric conditions: T –phase with the structure of thenardite, γ'' –phase with the structure of rhombic burkeite, χ –phase with the structure of soda monohydrate

Figure 1: Fig. 2. Phase-equilibrium diagram of melts of the $\text{Na}_2\text{SO}_4\text{--Na}_2\text{CO}_3$ system in the presence of water vapor and under atmospheric conditions: T –phase with the structure of thenardite, γ'' –phase with the structure of rhombic burkeite, χ –phase with the structure of soda monohydrate

two-component to a three-component state, and the phase-equilibrium diagram of the binary system $\text{Na}_2\text{SO}_4\text{--Na}_2\text{CO}_3$ (Fig. 1) is transformed into the phase-equilibrium diagram of the ternary system $\text{Na}_2\text{SO}_4\text{--Na}_2\text{CO}_3\text{--H}_2\text{O}$ (Fig. 2).

Institute of Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

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