STUDY OF SOLID-PHASE REACTION BETWEEN CsNO₃ AND V₂O₅ IN THE MOLAR RATIO 6 : 5

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Using DTA, DTG and TG methods, the solid-phase reaction between CsNO₃ and V₂O₅ in the molar ratio 6 : 5 has been studied in oxygen and air streams in the temperature range 20 — 550 °C. The reaction proceeds stepwise and CsV₃O₈ has been identified as an intermediate. A mixture of CsVO₃ and Cs₂V₄O₁₁ is formed as final product of the reaction at 520 °C. The composition of this mixture does not change up to 1000 °C.

The solid-phase reactions in V₂O₅ — alkaline metal salt systems have been investigated and various phase diagrams have been constructed in many papers. The essential results of these papers are summarized in the monograph of Fotiev and Ivakin [1].

It is possible to use solid-phase reactions under defined conditions even for preparation of certain polyvanadates, e.g. pentavanadates. K₃V₅O₁₄ was prepared by the reaction of KNO₃ and V₂O₅ in the appropriate ratio at 500 °C [2], and identified in the KVO₃ — V₂O₅ system [3]. Similarly, Rb₃V₅O₁₄ was identified in the RbVO₃ — V₂O₅ system [4]. The above pentavanadates may be obtained by the reactions of V₂O₅ with the corresponding metal nitrates or carbonates, respectively in the appropriate stoichiometric ratio [1]. Thus, Tl₃V₅O₁₄ was obtained from the solid-phase reaction of TlNO₃ and V₂O₅ at 550 °C [5]. Caesium pentavanadate has not been unambiguously proved to exist; its existence was not indicated by the phase diagram of Cs₂CO₃(Cs₂O) — V₂O₅ [1, 6, 7]. On the other hand, the possibility of its preparation by the dehydration of Cs₈V₁₀O₂₈·xH₂O has been mentioned [8].

The solid-phase reaction between CsNO₃ and V₂O₅ in the molar ratio corresponding to pentavanadate was studied so as to ascertain the possibility of caesium pentavanadate preparation.

Experimental

V₂O₅ was prepared by the thermal decomposition of NH₄VO₃ in an oxygen stream. CsNO₃ was recrystallized three times. The substances were dried at 120 °C before reaction and sieved through a sieve with 4900 mesh/cm². The mixture of CsNO₃ + V₂O₅ in the molar ratio 6 : 5 was prepared just before the reaction. Measurements were made in a Pt crucible or on Pt-plates in an air or an oxygen stream, with a derivatograph (MOM, Hungary). The weighed amounts of mixtures...
were 600 mg on Pt plates and 300 mg in a Pt crucible, respectively. The temperature ranges varied (max. 20—1000°). Sensitivities: DTA 1/5, DTG 1/10, TG 100 mg; heating-rate 5°/min.

The products obtained at various temperature were left to cool to 20° in a suitable stream and identified by X-ray phase-analysis Phillips X-ray diffractometer, PW 1058 goniometer, CuKα radiation, by I.R. spectroscopy (Perkin Elmer 567 instrument) using the nujol technique, and by chemical analysis. Caesium was determined by flame-photometry (Flame-photometer III, C. Zeiss, Jena), vanadium(V) was determined volumetrically, and vanadium (IV) was detected by E.P.R. (E.P.R. spectrometer ER-9, C. Zeiss, Jena).

**Results and discussion**

**Thermal synthesis**

The thermal curves of the reaction between CsNO₃ and V₂O₅ in the molar ratio 6 : 5 in an air stream are shown in Figs 1 and 2.

The endothermic process with maximum at 152° (Fig. 1) is connected with the structural transformation of CsNO₃; this was also found in the DTA curve of CsNO₃. The weight loss starts at 235°. The further courses of the DTA, DTG and TG curves indicate the gradual character of the reaction. The course of the reaction was studied on Pt plates in order to obtain a better differentiation of the individual

![Graph](image)

Fig. 1. TG, DTG and DTA curves of the reaction performed in a Pt crucible

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