

PHASE EQUILIBRIA IN THE SYSTEM $\text{FeVO}_4\text{-Fe}_2\text{WO}_6$ IN THE SOLID STATE

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Abstract

A diagram of the phase equilibria established in the solid state in the system $\text{FeVO}_4\text{-Fe}_2\text{WO}_6$ was plotted on the basis of X-ray phase analysis and DTA. This system, one of the intersections of the three-component system $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5\text{-WO}_3$, does not appear to be a real two-component system in the solid state.

Keywords: $\text{FeVO}_4\text{-Fe}_2\text{WO}_6$ system, phase equilibria

Introduction

The noteworthy catalytic properties of certain transition metal oxides and their mixtures make multicomponent systems of such oxides an interesting subject of investigation, as concerns both the phase equilibria established in the systems and the formation of new chemical compounds. In depth studies were earlier performed on the phase equilibria established in the systems $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5\text{-MoO}_3$ [1] and $\text{Cr}_2\text{O}_3\text{-V}_2\text{O}_5\text{-MoO}_3$ [2, 3]. Our attention has now turned to the hitherto unknown system $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5\text{-WO}_3$, whose components and their mixtures display catalytic properties, e.g. Fe_2O_3 or mixtures of Fe_2O_3 and V_2O_5 are used in the oxidation of methanol [4], mixtures of V_2O_5 and WO_3 catalyse the reduction of cyclohexane [5], and the synthesis of ammonia is catalysed by Fe_2WO_6 [6].

The three-component system $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5\text{-WO}_3$ may be regarded as a system built up from three two-component systems: $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5$, $\text{V}_2\text{O}_5\text{-WO}_3$ and $\text{Fe}_2\text{O}_3\text{-WO}_3$. The phase equilibria established in the first of these systems, and also the formation conditions for iron(III) vanadates(V), have been investigated thoroughly [7]. A literature survey concerning the second two-component system merely revealed that, when heated in air at ambient pressure, its components form a solid solution of WO_3 in V_2O_5 with a 7% mol solubility limit [5, 8]. Diagrams of the phase equilibria of the third two-component system, $\text{Fe}_2\text{O}_3\text{-WO}_3$, published before we commenced our investigations, indicated that

only one compound, Fe_2WO_6 , was formed in the system [9, 10], but there was no uniformity as regards the temperature and mode of melting of Fe_2WO_6 . Gardiner and Chang [9] maintained that Fe_2WO_6 melts congruently at $1142\pm 5^\circ\text{C}$, whereas Trumm [10] stated that the compound melts incongruently at $1156\pm 4^\circ\text{C}$ to deposit $\alpha\text{-Fe}_2\text{O}_3$. Our screening tests on the system $\text{Fe}_2\text{O}_3\text{-WO}_3$ confirmed that Fe_2WO_6 melts incongruently, depositing $\alpha\text{-Fe}_2\text{O}_3$, but at $1100\pm 10^\circ\text{C}$.

The current work covers the subject of the phase equilibria established in the solid state in the system $\text{FeVO}_4\text{-Fe}_2\text{WO}_6$, one of the sections of the three-component system $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5\text{-WO}_3$.

Iron(III) orthovanadate, one of the two compounds formed in the system $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5$ [7], crystallizes in a triclinic system [12] and melts incongruently at $850\pm 5^\circ\text{C}$, yielding solid $\alpha\text{-Fe}_2\text{O}_3$ [7]. FeVO_4 exhibits no polymorphism at ambient pressure, but a high-pressure polymorphic variety is known [13].

Fe_2WO_6 , the only compound arising in the system $\text{Fe}_2\text{O}_3\text{-WO}_3$ [9-11], is reported to exhibit two polymorphic varieties [14, 15]. A low-temperature variety with a columbite structure has been obtained in synthesis conducted at $800\text{-}850^\circ\text{C}$ from an equimolar mixture of the oxides [14, 15]. A high-temperature variety with $\alpha\text{-PbO}_2$ structure has been obtained in synthesis carried out from the oxides at $900\text{-}1000^\circ\text{C}$ [14-16], or as a product of the monotropic transformation of the low-temperature variety of Fe_2WO_6 at above 950°C [14]. Our studies on iron(III) tungstate have shown that synthesis at $650\text{-}840^\circ\text{C}$ initially leads to $\alpha\text{-Fe}_2\text{WO}_6$ with a columbite structure, which on long-term heating in the same temperature range undergoes monotropic transformation to a new polymorphic variety, $\beta\text{-Fe}_2\text{WO}_6$, distinguished by crystallizing in a monoclinic system [17]. Above 950°C , $\beta\text{-Fe}_2\text{WO}_6$ is transformed enantiotropically into $\gamma\text{-Fe}_2\text{WO}_6$ with the $\alpha\text{-PbO}_2$ structure [17]. Experimental results of individual investigations of the reactivity of Fe_2WO_6 in the system $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5\text{-WO}_3$ suggest that a solid solution of V_2O_5 is formed in all three polymorphic Fe_2WO_6 varieties in this system [18].

Experimental

Analar $\alpha\text{-Fe}_2\text{O}_3$ (VEB, Germany) calcined at 1000°C in three 24-h heating cycles, analar V_2O_5 (POCh, Poland) and analar WO_3 (Fluka AG, Switzerland) calcined at 700°C for 24 h were used for measurements.

Mixtures of the oxides, weighed in appropriate proportions, were homogenized by grinding, shaped into pastilles and then heated in air at chosen (in screening tests) temperatures within fixed time cycles. 20 samples with the compositions shown in the Table were prepared for experiments. The samples were heated as follows:

550°C (24 h) + 600°C (48 h) + 650°C (48 h) + 700°C
(24 h + 48 h + 2×120 h + 144 h) + 720°C (2×120 h).

After each heating cycle, the samples were cooled to ambient temperature, ground down, examined by DTA and X-ray phase analysis, then re-shaped into pastilles and subjected to further heating. As confirmation of equilibrium, the phase compositions of the preparations after two successive heating cycles at the given temperature remained unchanged.

In order to specify the nature of the phases existing in preparations formed from initial mixtures with an 80.00% mol or higher content of Fe_2WO_6 , the preparations were additionally heated for 5 h at 780, 800, 840, 880 and 900°C, then cooled rapidly to ambient temperature, ground down and examined by X-ray phase analysis.

The phase compositions of the preparations were established by means of their X-ray powder diffraction patterns recorded with a DRON-3 diffractometer Russia and filtered $\text{CoK}\alpha$ radiation. The phases were identified on the basis of the index data listed on PDF cards [19] and in publications [15–17].

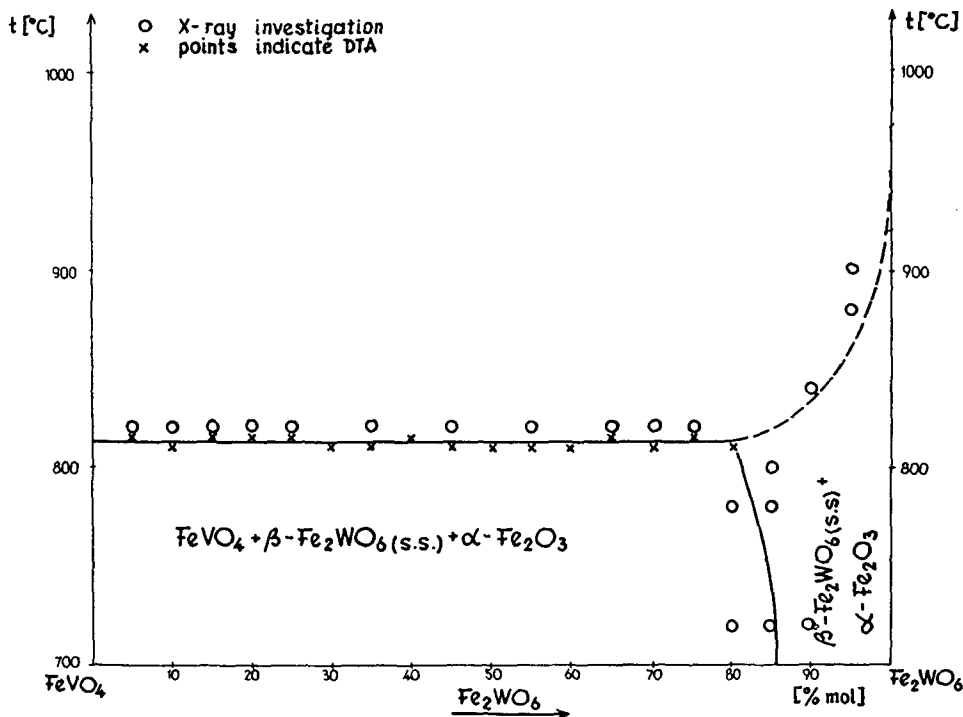


Fig. 1 Diagram of the phase equilibria in the solid-state and $\text{FeVO}_4\text{-Fe}_2\text{WO}_6$ system

Table 1 Compositions of initial mixtures and X-ray phase analysis of preparations being at equilibrium in the $\text{FeVO}_4\text{-Fe}_2\text{WO}_6$ system

| No. | Compositions of initial mixtures / % mol | | | | Phase composition of equilibrium samples* |
|-----|--|------------------------|---------------|---|---|
| | Fe_2O_3 | V_2O_5 | WO_3 | Fe_2WO_6 in terms of comp. system | |
| 1 | 50.00 | 45.24 | 4.76 | 5.00 | $\text{FeVO}_4, \beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \alpha\text{-Fe}_2\text{O}_3$ |
| 2 | 50.00 | 40.91 | 9.09 | 10.00 | $\text{FeVO}_4, \beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \alpha\text{-Fe}_2\text{O}_3$ |
| 3 | 50.00 | 36.95 | 13.05 | 15.00 | $\text{FeVO}_4, \beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \alpha\text{-Fe}_2\text{O}_3$ |
| 4 | 50.00 | 33.33 | 16.67 | 20.00 | $\text{FeVO}_4, \beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \alpha\text{-Fe}_2\text{O}_3$ |
| 5 | 50.00 | 30.00 | 20.00 | 25.00 | $\text{FeVO}_4, \beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \alpha\text{-Fe}_2\text{O}_3$ |
| 6 | 50.00 | 26.92 | 23.08 | 30.00 | $\text{FeVO}_4, \beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \alpha\text{-Fe}_2\text{O}_3$ |
| 7 | 50.00 | 24.07 | 25.93 | 35.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \text{FeVO}_4, \alpha\text{-Fe}_2\text{O}_3$ |
| 8 | 50.00 | 21.43 | 28.57 | 40.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \text{FeVO}_4, \alpha\text{-Fe}_2\text{O}_3$ |
| 9 | 50.00 | 18.97 | 31.03 | 45.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \text{FeVO}_4, \alpha\text{-Fe}_2\text{O}_3$ |
| 10 | 50.00 | 16.67 | 33.33 | 50.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \text{FeVO}_4, \alpha\text{-Fe}_2\text{O}_3$ |
| 11 | 50.00 | 14.52 | 35.48 | 55.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \text{FeVO}_4, \alpha\text{-Fe}_2\text{O}_3$ |
| 12 | 50.00 | 12.51 | 37.49 | 60.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \text{FeVO}_4, \alpha\text{-Fe}_2\text{O}_3$ |
| 13 | 50.00 | 10.61 | 39.39 | 65.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \text{FeVO}_4, \alpha\text{-Fe}_2\text{O}_3$ |
| 14 | 50.00 | 10.00 | 40.00 | 66.67 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \text{FeVO}_4, \alpha\text{-Fe}_2\text{O}_3$ |
| 15 | 50.00 | 8.83 | 41.17 | 70.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \text{FeVO}_4, \alpha\text{-Fe}_2\text{O}_3$ |
| 16 | 50.00 | 7.14 | 42.86 | 75.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \text{FeVO}_4, \alpha\text{-Fe}_2\text{O}_3$ |
| 17 | 50.00 | 5.55 | 44.45 | 80.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \text{FeVO}_4, \alpha\text{-Fe}_2\text{O}_3$ |
| 18 | 50.00 | 4.06 | 45.94 | 85.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \alpha\text{-Fe}_2\text{O}_3$ |
| 19 | 50.00 | 2.63 | 47.37 | 90.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \alpha\text{-Fe}_2\text{O}_3$ |
| 20 | 50.00 | 1.28 | 48.72 | 95.00 | $\beta\text{-Fe}_2\text{WO}_{6(s.s.)}, \alpha\text{-Fe}_2\text{O}_3$ |

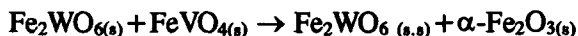
*Succession in records has resulted from the decreasing phase contents

DTA records of the preparations were made with a Paulik-Paulik-Erdey derivatograph (MOM, Budapest). Samples with a mass of 1000 mg were heated in quartz crucibles in air at a heating rate of 10 deg/min.

Results and discussion

The Table gives the compositions of the initial mixtures and the X-ray phase analysis results after the final cycle of the heating. The tabulated data show that the components of the system under study do not remain at permanent mutual equilibrium. This is proved by the occurrence of $\alpha\text{-Fe}_2\text{O}_3$ in all the preparations, and by the lack of FeVO_4 , one of the components of the system, in preparations obtained from initial mixtures containing the equivalent of 85.00% mol

or more Fe_2WO_6 . Such a phase composition is in accordance with our earlier observations [18] that a solid solution of V_2O_5 in iron(III) tungstate occurs in the system Fe_2O_3 – V_2O_5 – WO_3 :



The first endothermic effect in the DTA curves of preparations obtained at 720 °C from initial mixtures containing up to 80.00% mol Fe_2WO_6 was recorded at 810–815°C. The effect indicates melting of a triple eutectic at this temperature. The occurrence of this eutectic has also been observed in the system FeVO_4 – WO_3 [11].

The Figure shows a diagram of the phase equilibria of the system FeVO_4 – Fe_2WO_6 in the solid state. The course of full lines was determined on the basis of DTA and X-ray phase analysis results, whereas the broken line was plotted merely on the basis of X-ray phase analysis.

It follows from the diagram that the system FeVO_4 – Fe_2WO_6 , one of the intersections of the three-component system Fe_2O_3 – V_2O_5 – WO_3 , is not a real two-component system, not even in the solid state.

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Zusammenfassung — Auf der Grundlage von Röntgen-Phasenanalyse und DTA wurde ein Diagramm des Phasengleichgewichtes aufgezeichnet, welches im festen Zustand des Systemes

$\text{FeVO}_4\text{-Fe}_2\text{WO}_6$ nachgewiesen wurde. Dieses System, einer der Zwischenbereiche im Dreikomponentensystem $\text{Fe}_2\text{-V}_2\text{O}_5\text{-WO}_3$, scheint im festen Zustand kein echtes Zweikomponentensystem zu sein.