# PHASE EQUILIBRIA IN THE SYSTEM $Fe_2O_3$–$V_2O_5$–$WO_3$ IN THE SOLID STATE

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## Abstract

DTA and X-ray phase diffraction methods were used to construct a solidus area projection onto the component concentration triangle plane of the system $Fe_2O_3$–$V_2O_5$–$WO_3$.

**Keywords**: DTA, phase equilibria, system $Fe_2O_3$–$V_2O_5$–$WO_3$

## Introduction

Literature studies indicate that, in contrast with two-component systems of metal oxides, three-component systems have not received as much comprehensive research attention. These systems arouse great interest in consequence of the phase equilibria established in such materials and the kinetics of reactions taking place in them. Reactions that occur in three-component systems may lead to phases not previously known. We recently made a detailed study of the hitherto rather neglected three-component system $Fe_2O_3$–$V_2O_5$–$WO_3$; the components and their mixtures, and some of the compounds occurring in this system have been introduced into practical use, mainly as catalysts, in a variety of chemical processes. The three-component system $Fe_2O_3$–$V_2O_5$–$WO_3$ is built up of three two-component systems: $Fe_2O_3$–$V_2O_5$, $V_2O_5$–$WO_3$ and $Fe_2O_3$–$WO_3$. Verification studies have confirmed the literature data on two of the systems, i.e. $Fe_2O_3$–$V_2O_5$ and $V_2O_5$–$WO_3$ [1, 2]. In the third system, $Fe_2O_3$–$WO_3$, only one compound is formed in the solid state, viz. $Fe_2WO_6$. Our investigations permit the statement that iron(II) tungstate occurs not in two polymorphic forms, as believed so far, but in three forms [3]. When synthesis is carried out at 650–840°C, the first compound to occur will be $\alpha$-$Fe_2WO_6$, with a columbite structure, which after prolonged heating in this temperature range undergoes monotropic transformation to yield a novel $\beta$-$Fe_2WO_6$ modification that crystallizes in a monoclinic system [3]. Above 950°C, $\beta$-$Fe_2WO_6$ undergoes enantiotropic change into $\gamma$-$Fe_2WO_6$, which has a structure of tri-$\alpha$-$PbO_2$ type [3, 4].

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Careful investigation of the three-component system $Fe_2O_3$–$V_2O_5$–$WO_3$ indicates that all three components of the system are involved in the formation of a novel compound, to which the molecular formula $Fe_8V_{10}W_{16}O_{85}$ has been attributed [5]. This compound melts incongruently at 830±5°C, depositing two products: $Fe_2WO_6$ and $WO_3$ [5]. Further findings reveal that a solid solution of $V_2O_5$ in $Fe_2WO_6$ is also formed in the system [6]. The results of studies on the title system have permitted the elaboration of some diagrams of phase equilibria established in certain two-component systems, these being sections of the three-component system of interest, i.e. in $FeVO_4$–$WO_3$ [7], $Fe_2WO_6$–$FeVO_4$ [8], $Fe_2V_4O_{13}$–$WO_3$ [9], $V_2O_5$–$Fe_2WO_6$ [10], $Fe_8W_{16}O_{85}$–$Fe_2O_3$ and $Fe_8V_{10}W_{16}O_{85}$–$Fe_2WO_6$ [11] and $V_2O_5$–$Fe_8V_{10}W_{16}O_{85}$ [12].

The present work includes verification of the conclusions inferred from the earlier studies on the phase equilibria established in the above-mentioned two-component systems, which exist as sections of the system $Fe_2O_3$–$V_2O_5$–$WO_3$. In effect, the new experimental data allowed a solidus area projection onto the component concentration triangle plane of the system under consideration.

## Experimental

The following reagents were used for the experiments: $\alpha$-$Fe_2O_3$ (Analar, VEB, Laborchemie Apolda, Germany), further calcined at 1000°C in 3×24 h stages; $V_2O_5$ (Analar, POCh, Gliwice, Poland); $WO_3$ (Analar, Fluka AG, Switzerland) further calcined at 700°C for 24 h; $FeVO_4$, prepared according to the procedure in [1]; $Fe_2V_4O_{13}$, prepared according to the procedure in [1]; $Fe_8V_{10}W_{16}O_{85}$, prepared according to the procedure in [5] and $\beta$-$Fe_2WO_6$, prepared according to the procedure [3].

For the verification experiments, 14 samples were prepared as mixtures of the phases earlier found to exist in equilibrium in the given area. Shaped into pastilles, the mixtures were heated for 24 h at a temperature lower than the corresponding solidus line temperature by ca 20°C, and then cooled quickly to ambient temperature. The samples were then ground and examined by DTA and XRD methods.

The natures of the phases occurring in the samples were established via the powder diffraction patterns obtained with a DRON-3 X-ray diffractometer (Bourevestnik, Sankt Petersbourg, Russia). A cobalt lamp ($CoK_{\alpha}$) with an Fe filter was used as a radiation source. Phase identification was based on the X-ray characteristics included in the PDF cards [13] and on those published [5, 12].

DTA measurements were carried out with a Paulik-Paulik-Erdey derivatograph (MOM, Budapest, Hungary). The measurements were made in air, over the temperature range 20–1000°C. Weighed samples of 1000 mg were heated in quartz crucibles at a heating rate of 10°C $min^{-1}$. A ±5°C degree of accuracy of thermal effect temperature readings in the DTA curves was established by achieving the repeatability of the results in screening tests.

# Results and discussion

Table 1 details the contents of the verification samples and the natures of the phases in equilibrium. The results obtained confirmed the conclusions inferred from the earlier studies on the phase equilibria established in the two-component systems that are sections of the three-component system $Fe_2O_3$–$V_2O_5$–$WO_3$.

**Table 1** Results of X-ray phase analysis of verification samples

| Contents of verification samples in terms of components of the system $Fe_2O_3$–$V_2O_5$–$WO_3$/mol% | | | Natures of phases found in equilibrium samples |
|---|---|---|---|
| $Fe_2O_3$ | $V_2O_5$ | $WO_3$ | |
| 53.00 | 2.00 | 45.00 | $\beta$-$Fe_2WO_{6(s.s.)}$, $\alpha$-$Fe_2O_3$ |
| 43.00 | 2.00 | 55.00 | $\beta$-$Fe_2WO_{6(s.s.)}$, $WO_3$ |
| 45.00 | 5.00 | 50.00 | $Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, $V_2O_5$ |
| 25.00 | 65.00 | 10.00 | $Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, $V_2O_5$ |
| 30.00 | 40.00 | 30.00 | $Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, $FeVO_4$ |
| 40.00 | 50.00 | 10.00 | $Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, $FeVO_4$ |
| 60.00 | 20.00 | 20.00 | $\beta$-$Fe_2WO_{6(s.s.)}$, $FeVO_4$, $\alpha$-$Fe_2O_3$ |
| 80.00 | 10.00 | 10.00 | $\beta$-$Fe_2WO_{6(s.s.)}$, $FeVO_4$, $\alpha$-$Fe_2O_3$ |
| 45.00 | 10.00 | 45.00 | $Fe_8V_{10}W_{16}O_{85}$, $\beta$-$Fe_2WO_{6(s.s.)}$, $FeVO_4$ |
| 35.00 | 25.00 | 40.00 | $Fe_8V_{10}W_{16}O_{85}$, $\beta$-$Fe_2WO_{6(s.s.)}$, $FeVO_4$ |
| 15.00 | 5.00 | 80.00 | $Fe_8V_{10}W_{16}O_{85}$, $\beta$-$Fe_2WO_{6(s.s.)}$, $WO_3$ |
| 20.00 | 10.00 | 70.00 | $Fe_8V_{10}W_{16}O_{85}$, $\beta$-$Fe_2WO_{6(s.s.)}$, $WO_3$ |
| 10.00 | 20.00 | 70.00 | $Fe_8V_{10}W_{16}O_{85}$, $V_2O_5$, $WO_3$ |
| 5.00 | 45.00 | 50.00 | $Fe_8V_{10}W_{16}O_{85}$, $V_2O_5$, $WO_3$ |
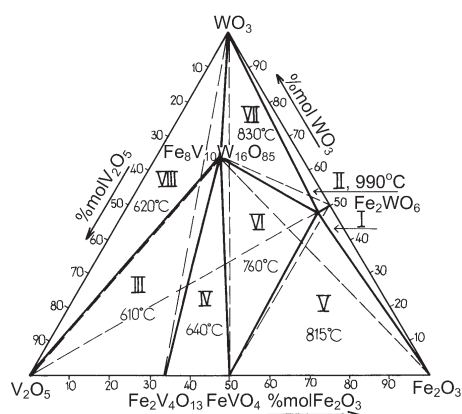


**Fig. 1** Projection of solidus area onto the component concentration triangle plane of the system $Fe_2O_3$–$V_2O_5$–$WO_3$

The data allowed a solidus area projection to be drawn onto the component concentration triangle plane of the given system, the projection showing concentration ranges for the components of the system, including phases which are in equilibrium in the solid state (Fig. 1). The dotted lines in the Figure indicate two-component systems for which phase equilibrium diagrams have been established. The experiments permitted determination of the processes involved in the melting of the particular phase mixtures.

Areas I and II depict the component concentration ranges for the system in which two phases are in equilibrium:

area I:     $\alpha$-$Fe_2O_3$ and $\beta$-$Fe_2WO_{6(s.s.)}$, melting temperature >1000°C,
area II:    $WO_3$ and $\beta$-$Fe_2WO_{6(s.s.)}$, a eutectic melting at 990±5°C.

Areas III and VIII reveal the component concentration ranges within which three phases are in equilibrium, their mixture melting as a eutectic:

area III:   $V_2O_5$, $Fe_8V_{10}W_{16}O_{85}$ and $Fe_2V_4O_{13}$, melting temperature 610±5°C,
area VIII:  $V_2O_5$, $Fe_8V_{10}W_{16}O_{85}$ and $WO_3$, melting temperature 620±5°C.

The other areas relate to the component concentration ranges of the given system which involve three solid phases in equilibrium, their mixture melting as a peritectic:

area IV:    $Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$ and $FeVO_4$, melting temperature 640±5°C,
area V:     $FeVO_4$, $\beta$-$Fe_2WO_{6(s.s.)}$ and $\alpha$-$Fe_2O_3$, melting temperature 815±5°C,
area VI:    $FeVO_4$, $\beta$-$Fe_2WO_{6(s.s.)}$ and $Fe_8V_{10}W_{16}O_{85}$, melting temperature 760±5°C,
area VII:   $\beta$-$Fe_2WO_{6(s.s.)}$, $Fe_8V_{10}W_{16}O_{85}$ and $WO_3$, melting temperature 830±5°C.

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