# SUBSOLIDUS PHASE EQUILIBRIA IN THE $V_9Mo_6O_{40}$–$Cr_2(MoO_4)_3$ SYSTEM

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## Abstract

The $V_9Mo_6O_{40}$–$Cr_2(MoO_4)_3$ system has been investigated using the differential thermal analysis (DTA) and X-ray phase diffraction methods. The system has been found not to be a real two-component system over the whole component system.

## Introduction

The compounds: $V_9Mo_6O_{40}$ and chromium(III) molybdate are still the objects of comprehensive studies on account of their interesting catalytic properties. Thus it seemed advisable to investigate the kinds of solid phases that coexist at equilibrium in the system built by the system components over the whole concentration range.

The $V_9Mo_6O_{40}$–$Cr_2(MoO_4)_3$ system is one of the sections of the three-component system of oxides: $Cr_2O_3$–$V_2O_5$–$MoO_3$. $V_9Mo_6O_{40}$ is a compound crystallizing in the two-component $V_2O_5$–$MoO_3$ system in which exists the substitution solid solution of $MoO_3$ in $V_2O_5$, too [1–6]. We have found that $V_9Mo_6O_{40}$ melts congruently at $640\pm10°C$ [7] whereas by other authors its melting temperature fluctuates between 635 and 677°C [1, 4–6]. Density of the phase is 3.86 g/cm$^3$ [5].

The properties and the structure of chromium(III) molybdate – of the other component of the system under study, are also known well. It has been found that $Cr_2(MoO_4)_3$ exists in two polymorphous modifications: a low-temperature modification crystallizing in a monoclinic system and a high-temperature that crystallizes in an orthorhombic system [8]. The structures of both the chromium(III) molybdate forms are known [9]. It is also known that $Cr_2(MoO_4)_3$ decomposes to $Cr_2O_3$ and $MoO_3$, molybdenum(VI) oxide sublimating simultaneously [10]. The decomposition starts at 810 °C yet at a very small rate.

Our earlier investigations showed that, when in the solid state, $Cr_2(MoO_4)_3$ did not react with the compound $CrVMoO_7$ [11], that is, with a compound

which crystallizes in the three-component $Cr_2O_3-V_2O_5-MoO_3$ system [12]. Likewise, $V_9Mo_6O_{40}$ in the solid state remained inert towards $CrVMoO_7$ [13].

## Experimental

In order to complete the study of phase equilibria being established in the solid state there were prepared, from $Cr_2O_3$, $V_2O_5$ and $MoO_3$, 20 samples with their compositions covering the whole component concentration range of the system under study. Oxide mixtures with given compositions were homogenized by grinding, shaping into pastilles and then heated in cycles under conditions that would ensure obtention of preparations remaining in the equilibrium state. Thus samples with the $Cr_2(MoO_4)_3$ content of up to 81.82 mol% in terms of the system components were heated at the following conditions:

$$400°C \rightarrow 500°C(24\ h) \rightarrow 550°C(2\times24\ h) \rightarrow 570°C(2\times24\ h)$$

On the other hand, the sample comprising 81.82 mol% of $Cr_2(MoO_4)_3$ and samples with the other concentration values for the components were heated as follows:

$$400°C \rightarrow 500°C(24\ h) \rightarrow 550°C(2\times24\ h) \rightarrow 600°C(2\times24\ h)$$
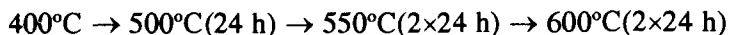
After each heating cycle, the samples were cooled to ambient temperature, ground down, reshaped into pastilles and heated until the equilibrium state was established in the preparations. The conditions for the equilibrium state establishment were determined by introductory tests made with samples that contained in their initial mixtures 25.00; 50.00; 81.82 and 90.00 mol% of $Cr_2(MoO_4)_3$, respectively, in terms of components of the investigated system. Establishment of the equilibrium state was verified by X-ray phase diffraction and DTA, made with selected samples after two successive calcination cycles. Two identical results were taken as indication of the established equilibrium state.

Diffraction patterns of the preparations were made using a diffractometer of a HZG-4/A2 type equipped with a cobalt lamp as a radiation source. Compositions of the preparations were determined by X-ray diffraction analysis, using the data listed in the PDF cards [14] and those included in publications [1, 12].

Differential thermal analysis (DTA) was made using a derivatograph of a Paulik-Paulik-Erdey type (MOM Budapest), in quartz crucibles, in air at 20–1000°C and a heating rate of 10 deg·min$^{-1}$. The weight of each sample was 1000 mg.

# Results and discussion

The Table shows the compositions of initial mixtures in terms of components of the investigated system, and the results of X-ray diffraction analysis for all the preparations in the equilibrium state.

The experimental results indicate that $Cr_2(MoO_4)_3$ does not remain, in sub-solidus area, in equilibrium with $V_9Mo_6O_{40}$. It follows from X-ray diffraction analysis that, up to 81.82 mol% of $Cr_2(MoO_4)_3$ in its contents, it is a mixture of three phases: $V_9Mo_6O_{40}$, $MoO_3$ and $CrVMoO_7$. The fact implies that up to that content, $Cr_2(MoO_4)_3$ reacts to completion to yield $CrVMoO_7$ and $MoO_3$. Thus at that concentration range, it is $CrVMoO_7$ and $MoO_3$, apart from $V_9Mo_6O_{40}$, that remain in equilibrium in the solid state.

Table 1 The compositions of initial mixtures and the results of X-ray diffraction analysis in the solid state

| No. | Composition of initial mixtures / mol% | | Phase composition of samples in the equilibrium state |
|---|---|---|---|
| | $Cr_2(MoO_4)_3$ | $V_9Mo_6O_{40}$ | |
| 1 | 2 | 3 | 4 |
| 1 | 5.00 | 95.00 | $V_9Mo_6O_{40}$, $MoO_3$, $CrVMoO_7$–traces |
| 2 | 10.00 | 90.00 | $V_9Mo_6O_{40}$, $MoO_3$, $CrVMoO_7$ |
| 3 | 20.00 | 80.00 | $V_9Mo_6O_{40}$, $MoO_3$, $CrVMoO_7$ |
| 4 | 25.00 | 75.00 | $V_9Mo_6O_{40}$, $MoO_3$, $CrVMoO_7$ |
| 5 | 30.00 | 70.00 | $V_9Mo_6O_{40}$, $MoO_3$, $CrVMoO_7$ |
| 6 | 40.00 | 60.00 | $V_9Mo_6O_{40}$, $MoO_3$, $CrVMoO_7$ |
| 7 | 45.00 | 55.00 | $V_9Mo_6O_{40}$, $MoO_3$, $CrVMoO_7$ |
| 8 | 50.00 | 50.00 | $V_9Mo_6O_{40}$, $MoO_3$, $CrVMoO_7$ |
| 9 | 60.00 | 40.00 | $V_9Mo_6O_{40}$, $MoO_3$, $CrVMoO_7$ |
| 10 | 65.00 | 35.00 | $MoO_3$, $CrVMoO_7$, $V_9Mo_6O_{40}$ |
| 11 | 70.00 | 30.00 | $MoO_3$, $CrVMoO_7$, $V_9Mo_6O_{40}$ |
| 12 | 75.00 | 25.00 | $MoO_3$, $CrVMoO_7$, $V_9Mo_6O_{40}$ |
| 13 | 80.00 | 20.00 | $MoO_3$, $CrVMoO_7$, $V_9Mo_6O_{40}$ |
| 14 | 81.82 | 18.18 | $MoO_3$, $CrVMoO_7$ |
| 15 | 82.50 | 17.50 | $MoO_3$, $CrVMoO_7$, $Cr_2(MoO_4)_3$ traces |
| 16 | 85.00 | 15.00 | $MoO_3$, $CrVMoO_7$, $Cr_2(MoO_4)_3$ |
| 17 | 87.50 | 12.50 | $MoO_3$, $CrVMoO_7$, $Cr_2(MoO_4)_3$ |
| 18 | 90.00 | 10.00 | $MoO_3$, $Cr_2(MoO_4)_3$, $CrVMoO_7$ |
| 19 | 92.50 | 7.50 | $MoO_3$, $Cr_2(MoO_4)_3$, $CrVMoO_7$ |
| 20 | 95.00 | 5.00 | $MoO_3$, $Cr_2(MoO_4)_3$, $CrVMoO_7$ |

A sample comprising 81.82 mol% of $Cr_2(MoO_4)_3$ in its initial mixture was a diphase in the equilibrium state and contained $CrVMoO_7$ and molybdenum(VI) oxide. Accordingly, one can state that at that concentration range in the solid state the following reaction takes place:

$$9Cr_2(MoO_4)_{3(s)} + 2V_9Mo_6O_{40(s)} + 1/2O_2 = 18CrVMoO_{7(s)} + 21MoO_{3(s)} \quad (1)$$
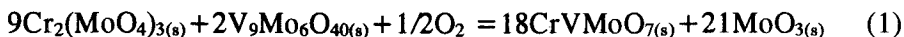
The reaction appears quantitative at 81.82 mol% of the $Cr_2(MoO_4)_3$ content. X-ray diffraction patterns of preparations at equilibrium which represent the other component concentration range of the system, viz. that of over 81.82 mol% of $Cr_2(MoO_4)_3$, has shown presence of three phases: $Cr_2(MoO_4)_3$, $CrVMoO_7$ and $MoO_3$. Phase compositions of the preparations is lacking $V_9Mo_6O_{40}$, which indicates that, at this component concentration range, chromium(III) molybdate is a phase occurring in excess against stoichiometric quantities following from reaction (1). The molybdate eventually remains in permanent equilibrium with the reaction products.
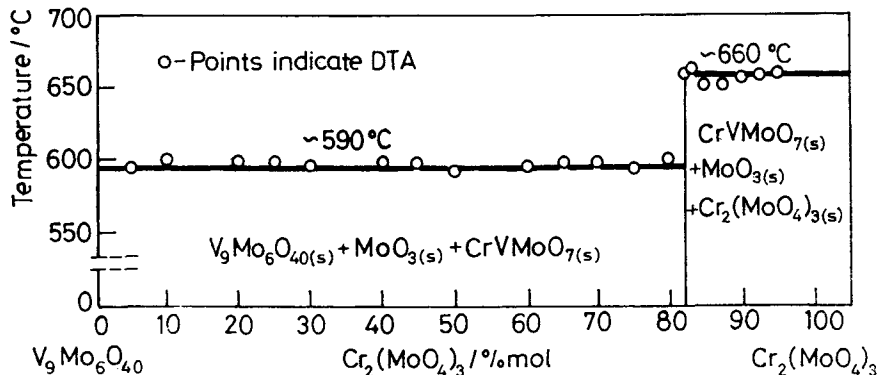


Fig. 1 Diagram of phase equilibria in the solid state of $V_9Mo_6O_{40}$–$Cr_2(MoO_4)_3$ system

Figure 1 shows phase equilibria in the solid state of $V_9Mo_6O_{40}$–$Cr_2(MoO_4)_3$ system. The temperature range for the subsolidus area has been established basing on the first effect onset temperatures recorded on the DTA curves of the preparations at equilibrium. The DTA curves for preparations with the $Cr_2(MoO_4)_3$ content of up to 81.82 mol% show the start of the first endothermic effect, recorded at 590±5°C. On the DTA curves for the preparations at equilibrium, representing the component concentration range of over 81.81 mol% of $Cr_2(MoO_4)_3$, the first effect onset temperature was established 660±5°C.

The experimental results presented indicate that $V_9Mo_6O_{40}$–$Cr_2(MoO_4)_3$ is not a real two-component system in the subsolidus area. The conclusion can be derived from the fact, that in both the fields separated below the solidus line, it is three solid phases that remain in equilibrium. Figure 2 shows the position of the $V_9Mo_6O_{40}$–$Cr_2(MoO_4)_3$ section on the concentration triangle for the three-
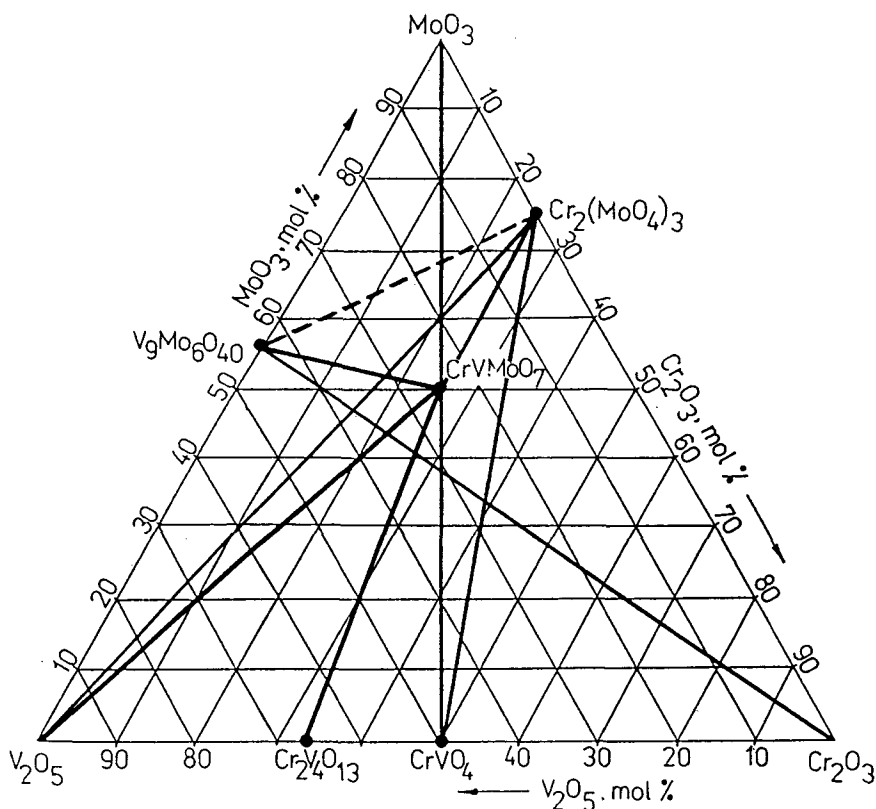
**Fig. 2** Component concentration triangle for $Cr_2O_3$–$V_2O_5$–$MoO_3$ system — the
$Cr_2O_3$–$V_2O_5$–$MoO_3$ sections under study ---- the $V_9Mo_6O_{40}$–$Cr_2(MoO_4)_3$ section

component $Cr_2O_3$–$V_2O_5$–$MoO_3$ system. The triangle shows also the sections of
the system studied previously.

## References

1 R. H. Munch and E. D. Pierron, J. Catal., 3 (1964) 406.
2 M. Eick and L. Kihlborg, Acta Chem. Scand., 20 (1966) 1658.
3 R. C. T. Slade, J. Solid State Chem., 82 (1989) 65.
4 A. Bielański, K. Dyrek, J. Poźniczek and E. Wenda, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 19 (1971) 507.
5 R. H. Jarman, P. G. Dickens and A. J. Jacobson, Mater. Res. Bull., 17 (1982) 325.
6 N. Strupler and A. Morette, Chim. Miner., 260 (1965) 1971.
7 J. Walczak, M. Kurzawa and P. Tabero, J. Thermal, Anal., 33 (1988) 969.
8 L. M. Plasova and L. M. Kefeli, Izv. Akad. Nauk SSSR, Neorg. Mater., 3 (1967) 906.
9 A. W. Sleight and L. H. Brixner, J. Solid State Chem., 7 (1973) 172.
10 J. Walczak, M. Kurzawa and E. Filipek, Thermochim. Acta, 150 (1989) 133.

11 J. Walczak and E. Filipek, Thermochim. Acta, 228 (1993) 127.
12 J. Walczak and E. Filipek, Thermochim. Acta, 150 (1989) 125.
13 J. Walczak and E. Filipek, Thermochim. Acta, 206 (1992) 279.
14 Joint Committee of Powder Diffraction; 5–508, 6–0504, 9–387, 16–256, 18–851, 19–813, 20–1377, 34–527.

**Zusammenfassung** — Mittels Differentialthermoanalyse (DTA) und Röntgendiffraktionsmethoden wurde das System $V_9Mo_6O_{40}$–$Cr_2(MoO_4)_3$ untersucht. Man fand, daß das System über das gesamte Komponentensystem kein wirkliches Zweikomponenten-System ist.