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PHASE EQUILIBRIA IN THE V_2O_5–Cr_2O_3 SYSTEM

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The phase equilibria in the total range of component concentrations in the V_2O_5–Cr_2O_3 system up to 1000 °C were studied by means of phase powder diffraction and DTA. Two compounds exist in the system: $CrVO_4$, melting incongruently at 860±5 °C, and $Cr_2V_4O_{13}$, which decomposes in the solid state at 640±5 °C to $CrVO_{4(s)}$ and $V_2O_{5(s)}$. At 645±5 °C, $CrVO_4$ and V_2O_5 form a eutectic mixture with the $CrVO_4$ content not exceeding 2% mol.

The two-component system of transition oxides V_2O_5–Cr_2O_3 has been the subject of many investigations primarily with respect to the catalytic properties of the phases in the system [1–12]. Catalysts of this type are used in the oxidation of organic compounds, e.g. of methanol to formaldehyde or benzene to maleic anhydride.

A literature study reveals that the result on the phase equilibria in the V_2O_5–Cr_2O_3 system differ essentially, even as concerns the number of phases in the system between 20 and 1000° [1–9]. Some authors [1–6] report that only one compound, $CrVO_4$, melting incongruently, exists in the system. Lucas and his associates report that the components of the system form two compounds, $CrVO_4$ and $Cr_2V_4O_{13}$ [7]. They inferred the existence of these compounds only from the liquidus line shape, without investigating the subsolidus area. Pletniev et al. studied the V_2O_5–Cr_2O_3 system by means of nuclear magnetic resonance [8]. Besides the signal corresponding to $CrVO_4$, they also observed a signal which they attributed to the phase $Cr_2V_4O_{13}$. However, they failed to obtain $Cr_2V_4O_{13}$ in a pure state. Accordingly, it was concluded that only one compound occurs in the system: $CrVO_4$. A phase diagram of the system of interest in the range of component concentrations 0–50% mol Cr_2O_3, which differs essentially from other elaborations, was presented by Olivier and Combe [9]. They reported not only $CrVO_4$, but two other compounds, $Cr(VO_3)_3$ and $Cr_4(V_2O_7)_3$, which were obtained by co-precipitation from appropriate solutions at precisely defined pH values. They stated

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that the compounds undergo irreversible decomposition to chromium orthovanadate and vanadium pentoxide. $Cr(VO_3)_3$ decomposes in this way at 566°, while $Cr_4(V_2O_7)_3$ does so at 592°. Olivier obtained $Cr_2V_4O_{13}$ by co-precipitation and found that it is stable only up to 566° [10]. Akifumi et al. produced catalysts containing Cr_2O_3 and V_2O_5 from ammonium metavanadate and chromium(III) nitrate. They obtained and isolated phases to which they ascribed the molecular formulae $Cr_2V_{12}O_{35}$ and $Cr_6V_{13}O_{45}$ [11].

$CrVO_4$ is a compound whose existence is confirmed by all workers dealing with the V_2O_5–Cr_2O_3 system [1–9]. They maintain that this compound melts incongruently, depositing a solid Cr_2O_3. The melting point of $CrVO_4$ has not been established so far, however. The various authors give 810° [1–2], 917° [3], 886° [4] and 902° [5–6]. Discrepancies between the literature data have been found as regards the composition and melting point of the eutectic mixture formed in the system [1–9]. Cirilli and Burdese reported that $CrVO_4$ forms a eutectic mixture with V_2O_5 with a composition corresponding to 77% mol V_2O_5 and 23% mol Cr_2O_3, the mixture melting at 665° [1–2]. On the other hand, Compleston et al. state that the eutectic mixture of $CrVO_4$ and V_2O_5 exists at a Cr_2O_3 content of below 1% mol, and melts at $668 \pm 5°$ [3]. The authors of other papers [4, 6, 9] are consistent in that the eutectic mixture contains below 1% mol Cr_2O_3, with melting point 650° [4], $667 \pm 5°$ [6] or $640 \pm 3°$ [9].

The present state of studies on the V_2O_5–Cr_2O_3 system induced us to undertake investigations with the aims of finding which of the compounds are stable phases in the system and under which conditions they coexist in stable equilibrium.

Experimental

V_2O_5 was a commercial product of p.a. grade, and Cr_2O_3 was obtained by thermal decomposition of $(NH_4)_2Cr_2O_7$, first at 100° and than at 150°. The product of decomposition was additionally calcined at 1000° for 72 h. Phase powder diffraction of the preparation showed that only Cr_2O_3 was present in the product.

The oxides (Table 1), weighed in appropriate amounts, were mixed by grinding, pastilling and calcining in air. Preparations with contents of up to 50% mol Cr_2O_3 were heated in the following cycles: 500° (24 h) — 550° (24 h) — 600° (24 h) — 630° (2 × 24 h) — 635° (24 h), whereas preparations containing above 50% mol Cr_2O_3 were heated at 500° (24 h) — 550° (24 h) — 600° (24 h) — 630° (24 h) — 700° (24 h) — 750° (24 h). In each heating cycle, the preparations were slowly cooled to ambient temperature, ground, subjected to differential thermal analysis and phase

Table 1 Phase compositions of initial mixtures and of preparations at equilibrium

Composition of initial mixtures, % mol Cr_2O_3	Phase composition of preparations at equilibrium
0.25; 0.5	V_2O_5, $Cr_2V_4O_{13}$ (traces)
0.75; 1; 3; 5; 7.5; 10; 14.3; 15; 20; 25; 30; 31.6	V_2O_5, $Cr_2V_4O_{13}$
33.33	$Cr_2V_4O_{13}$
35; 40; 45	$Cr_2V_4O_{13}$, ($CrVO_4$)
50	$CrVO_4$
55; 65; 70; 75; 85; 95	$CrVO_4$, Cr_2O_3

powder diffraction examinations, then freshly pastilled and heated to give a preparation in equilibrium.

The conditions under which equilibrium is established were found in screening tests, in which the conditions for synthesis of the phases existing in the V_2O_5–Cr_2O_3 system were also elaborated. The establishment of equilibrium was checked by phase powder diffraction of chosen specimens after two successive calcining cycles. If identical diffractograms were obtained, it was accepted that equilibrium had been achieved, the heating of the preparations was finished and the products were then analyzed.

DTA of the preparations was performed with a Paulik–Paulik–Erdey derivatograph (MOM, Budapest) in quartz crucibles in air at 20–1000° and a heating rate of 10 deg/min. The weighed amount of a preparation was 1000 mg in each case. The phase compositions of the specimens were assigned by using a DRON-3 diffractometer and a Co–K_α radiation source. The phases were identified with the help of appropriate ASTM cards and literature data [14, 15].

Results and discussion

It was found in the screening tests that there are two compounds in tme system, $CrVO_4$ and $Cr_2V_4O_{13}$. The phases $Cr(VO_3)_3$ and $Cr_4(V_2O_7)_3$, the existence of which was reported by Olivier and Combe [9], were not found, despite the long heating of mixtures of Cr_2O_3 and V_2O_5 with molar ratios corresponding to these oxides. Czesznicki et al. [6] stated that they too were unable to obtain these phases from the reaction between the oxides in the solid state. Neither did we find the formation of $Cr_2V_{12}O_{35}$ and $Cr_6V_{13}O_{45}$ in the solid state, although the existence of these compound was reported by Akifumi [11].

$CrVO_4$ was obtained by heating a mixture of Cr_2O_3 and V_2O_5 in a molar ratio of 1 : 1 under the following conditions: 500° (24 h) — 550° (24 h) — 600° (24 h) — 630° (24 h) — 700° (24 h) — 750° (24 h) — 800° (24 h).

Only reflections relating to $CrVO_4$ were recorded in the diffractograms of the preparations, their position being in accord with the data on the ASTM card [13].

$Cr_2V_4O_{13}$ was synthesized in the following way: a mixture of Cr_2O_3 and V_2O_5 in molar ratio of 1 : 2 was heted periodically at $635 \pm 5°$. The specimes were calcined for 3 h, ground and freshly pastilled. After four such cycles, preparations were obtained whose phase powder diffractograms did not show the presence of Cr_2O_3 or V_2O_5.

It was found that the set of diffraction lines characterizing $Cr_2V_4O_{13}$ include some which are common with the lines corresponding to $CrVO_4$, but the changes in their intensity during synthesis suggest that they also belong in the set of reflections characterizing $Cr_2V_4O_{13}$. If the preparation contained $CrVO_4$ besides $Cr_2V_4O_{13}$, its diffractogram would show reflections characteristic of V_2O_5.

In order to find in which concentration range V_2O_5 is detectable under the conditions of the measurements, screening tests were performed with physical mixtures with the compositions 97% mol $Cr_2V_4O_{13}$ + 3% mol V_2O_5, and 99% mol $Cr_2V_4O_{13}$ + 1% mol V_2O_5. Analysis showed that the mixture containing $Cr_2V_4O_{13}$ undoubtedly also contained 1% mol V_2O_5. Thus, the lack of lines characterizing V_2O_5 in the set of reflections recorded in the diffractograms of the preparations suggests that all the lines are attributable to the $Cr_2V_4O_{13}$ phase. Table 2 shows the X-ray characteristics of the phase elaborated on the basis of the

Table 2 Interplanar distances in $Cr_2V_4O_{13}$ and relative intensities corresponding to their reflections

d, Å	I, %	d, Å	I, %	d, Å	I, %
7.08	100	3.04	25	2.11	5
4.65	15	2.98	20	2.06	5
4.08	15	2.91	10	1.99	5
3.89	60	2.88	25	1.87	10
3.77	5	2.82	30	1.81	5
3.70	30	2.79	5	1.80	5
3.65	10	2.64	20	1.74	10
3.59	50	2.52	10	1.68	10
3.39	5	2.46	10	1.65	10
3.31	75	2.42	5	1.63	5
3.25	5	2.27	5		

diffractogram of the powder preparation, and Fig. 1 shows the DTA curves of $CrVO_4$ and $Cr_2V_4O_{13}$, respectively.

The dark-brown $CrVO_4$ melts incongruently, depositing solid Cr_2O_3, in agreement with the literature information [1–6]. On the other hand, the melting point of $CrVO_4$, measured repeatedly as the temperature of onset of the effect relating to the melting of the phase, was 860 ± 5° each time (Fig. 1, curve a). The other compound, with a reddish-brown colour $Cr_2V_4O_{13}$ remained stable when heated to 640 ± 5°. However, at above this temperature, it started to decompose in the solid phase, at an inconsiderable rate:

$$Cr_2V_4O_{13(s)} = 2CrVO_{4(s)} + V_2O_{5(s)}$$

At 740°, $Cr_2V_4O_{13}$ which had not undergone decomposition melted incongruently, depositing other portions of $CrVO_4$ (Fig. 1, curve b).

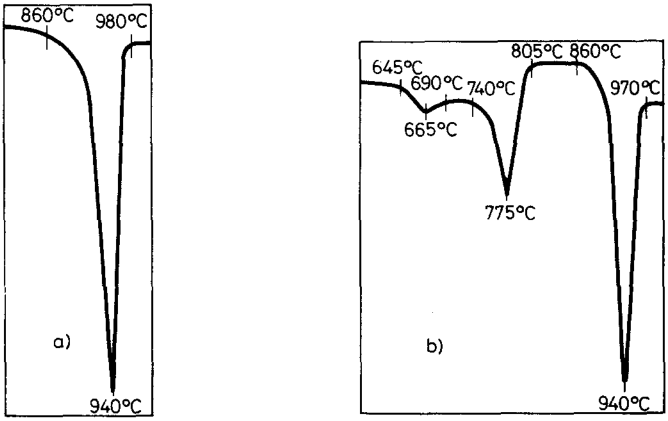

Fig. 1 DTA curves of $CrVO_4$ (a) and $Cr_2V_4O_{13}$ (b)

In order to establish the nature of the phases and the conditions under which they remain in stable equilibrium up to 1000° in the whole range of component concentrations, 25 specimens were prepared with the initial compositions given in Table 1. This Table also shows the phase compositions of the specimens on achieving equilibrium, i.e. after their heating under the given conditions. The phase diagram of the V_2O_5–Cr_2O_3 system in shown in Fig. 2. The ranges of coexistence for phases in equilibrium were determined by DTA, whereas the natures of phases existing in particular areas were established by phase powder diffraction (Table 1).

In order to confirm the correctness of the construction of the phase diagram above the solidus line in the range up to 50% mol Cr_2O_3, two kinds of tests were made. In the first test, preparations containing V_2O_5 and $Cr_2V_4O_{13}$ in equilibrium

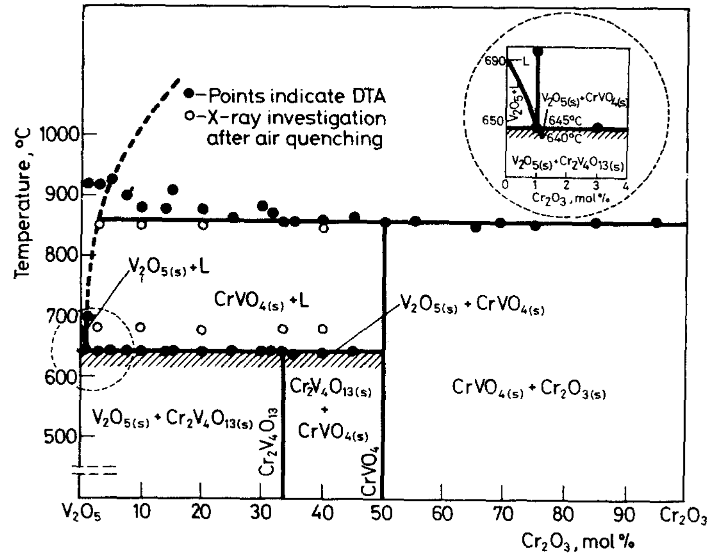

Fig. 2 Phase diagram of V_2O_5–Cr_2O_3 system

and corresponding to the initial mixtures with 3.00, 10.00 or 20.00% mol Cr_2O_3 were heated for 3 h at 850°, then cooled rapidly to ambient temperature and subjected to phase powder diffraction. The preparation containing $CrVO_4$ and $Cr_2V_4O_{13}$ in equilibrium, obtained from a mixture of oxides with 40.00% mol Cr_2O_3, was also subjected to such investigations. Phase powder diffraction of specimens after quenching showed that they were composed of $CrVO_4$ and V_2O_5. In the second test, the specimens were heated for 24 h at 680°. Phases were made from separately obtained $CrVO_4$ and V_2O_5, their compositions corresponding to 10.00, 20.00 and 33.33% mol Cr_2O_3 in the initial mixtures. In the case of two other phases, preparations were used which contained $Cr_2V_4O_{13}$ in equilibrium, i.e. 33.33% mol Cr_2O_3 in the initial mixture and $Cr_2V_4O_{13}$ and $CrVO_4$ with 40% mol Cr_2O_3. Phase powder diffraction of the five rapidly cooled preparations showed that they consisted of $CrVO_4$ and V_2O_5. Only in the case of specimens corresponding to 10.00 and 20.00% mol Cr_2O_3 were the reflections characterizing $Cr_2V_4O_{13}$ displaced and disfigured, which suggests that the phase crystallized from liquid. The compositions of specimens sed in these tests are indicated in the phase diagram of the system (Fig. 2).

It follows from the phase diagram that V_2O_5 and $Cr_2V_4O_{13}$ are in stable equilibrium up to 640° and at a content of 33.33% mol Cr_2O_3, whereas $Cr_2V_4O_{13}$ and $CrVO_4$ coexist at 33.33–50.00% mol Cr_2O_3. $Cr_2V_4O_{13}$ starts to decompose in the solid state at 640°. The eutectic point in this system undoubtedly occurs at a Cr_2O_3 content not exceeding 1% mol at 645°, $V_2O_{5(s)}$ and $CrVO_{4(s)}$ being phases in equilibrium with liquid. This fact was confirmed by additional experiments in which a mixture of V_2O_5 and separately obtained $CrVO_4$, with 2% mol $CrVO_4$ (1% mol Cr_2O_3), was prepared. The DTA of the ground mixture showed that the effect relating to the melting of the eutectic mixture is symmetrical and well-shaped. A small endothermic effect which corresponds to the melting of $CrVO_4$ was also recorded in this curve. A mixture of V_2O_5 and separately obtained $Cr_2V_4O_{13}$, containing 1% mol Cr_2O_3 (in terms of the system components), was also prepared. No effect relating to the melting of $Cr_2V_4O_{13}$ was recorded in the DTA curve, except for the effect!of melting of the eutectic mixture of $CrVO_4$ and V_2O_5 and a small effect of $CrVO_4$ melting. This result is in good accord with that observed for the equilibrium sample of the fundamental series (Table 1). Containing 1% mol Cr_2O_3 (in terms of the system components). The results obtained confirm the fact that the eutectic mixture contains Cr_2O_3 in amounts which do not exceed 1% mol of the oxide. The experimental results suggest that at slightly above 640° the decomposition of $Cr_2V_4O_{13}$ occurs and the resultant $CrVO_4$ forms an eutectic mixture with V_2O_5, existing at a temperature which differs only slightly from the temperature of $Cr_2V_4O_{13}$ decomposition. Thus, this fact can explain the existence of the first effect in the DTA curve of a preparation containing $Cr_2V_4O_{13}$ (Fig. 1, curve b).

The presented results allow the following conclusions:

1. Two compounds, $CrVO_4$ and $Cr_2V_4O_{13}$, exist in the V_2O_5–Cr_2O_3 system. $CrVO_4$ melts incongruently at 860 ± 5^c, depositing solid Cr_2O_3, whereas $Cr_2V_4O_{13}$ is stable up to $640 \pm 5°$, and at this temperature starts to decompose to $CrVO_4$ and V_2O_5 at an inconsiderable rate.

2. $Cr_2V_4O_{13}$ can be prepared through the reaction of Cr_2O_3 and V_2O_5 in the solid state. The X-ray characteristics of the phase were assigned in the angle range $2\theta = 12$–$70°$ (Co–K_α).

3. At $645 \pm 5°$, $CrVO_4$ and V_2O_5 from an eutectic mixture with $CrVO_4$ content not exceeding 2% mol of the compound.

4. The experimental results led to a phase diagram showing phase equilibria in the V_2O_5–Cr_2O_3 system up to 1000° in the whole range of component concentrations.

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Zusammenfassung — Mittels DTA und Pulverdiffraktionsaufnahmen wurde das Phasengleichgewicht des Systems V_2O_5–Cr_2O_3 bis 1000 °C im gesamten Konzentrationsbereich untersucht. Innerhalb des Systemes existieren zwei Verbindungen: $CrVO_4$ mit einem inkongruentem Schmelzpunkt bei 860 ± 5 °C und $Cr_2V_4O_{13}$, das sich in festem Zustand bei 640 ± 5 °C in $CrVO_{4(s)}$ und $V_2O_{5(s)}$ zersetzt. Bei 645 ± 5 °C bilden $CrVO_4$ und V_2O_5 ein eutektisches Gemisch mit einem maximalen $CrVO_4$-Gehalt von 2 mol%.

Резюме — Методом DTA и порошкого рентгенофазового анализа изучено фазовое равновесие системы V_2O_5–Cr_2O_3 до температуры 1000° и во всей области концентраций компонентов. Установлено наличие двух соединений: $CrVO_4$, плавящегося инконгруэнтно при 860 ± 5° и $Cr_2V_4O_{13}$, разлагающегося в твердом состоянии при 640 ± 5° до твердых $CrVO_4$ и V_2O_5, которые при температуре 645 ± 5° образуют эвтектическую смесь с содержанием $CrVO_4$, не превышающим 2 мольных %.