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Abstract

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On the Interaction of Uranium Oxides with Vanadium and Niobium Oxides

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The reactions of uranium oxides with vanadium oxides have been studied insufficiently thoroughly ($^{1-3}$), and with niobium oxides not at all. In the present work, methods of thermal and X-ray phase analysis were mainly used (aqueous vanadates and niobates were recorded in a Guinier focusing camera with a bent germanium crystal as monochromator). As a result of prolonged (85-100 h) boiling of aqueous suspensions of uranyl hydroxide and vanadium pentoxide, two new phases are formed. Uranyl pyrovanadate was found as the sole phase at the ratio $U : V = 1 : 1$—$2 : 3$, and hexavanadate at the ratio $U : V = 1 : 2$—$1 : 3^*$. Such broad regions of homogeneity in the "vanadates" seemed to us somewhat unexpected, and we attempted to apply other methods to determine the boundaries of the homogeneity regions. It proved impossible to apply the crystal-optical method because of the extremely small size of the crystals, and electron microscopy because the crystals lacked a clearly expressed faceting. The change in pH is significant on passing from the vanadate with $U : V = 1 : 1$ to $U : V = 1 : 2$. The pH values were found for suspensions with $U : V = 3 : 2$—5.50; $1 : 1$—5.25; $1 : 2$—4.30; $1 : 3$—3.05. These data agree with the pH values for sols (^{4}) with $U : V = 1 : 2$ (pH 4.28) and $U : V = 1 : 4$ (pH 3.37). The transition from uranyl hydroxide to pyrovanadate and from hexavanadate to vanadium pentoxide is not accompanied by a substantial change in pH, and the phase boundaries cannot be determined by this method. The infrared spectra of the pyrovanadate and hexavanadate proved to be different, which made it possible for us to use them for phase analysis. The identity of the IR spectra of vanadates with $U : V = 1 : 1$ and $2 : 3$, and also of vanadates with $U : V = 1 : 2$ and $1 : 3$, confirms the data of X-ray phase analysis. The presence of V_2O_5 in mixtures (for example, in the case of a preparation with $U : V = 1 : 6$) is also readily detected from the IR spectra, but the presence of uranyl hydroxide cannot be proved by this method (by X-ray diffraction it is detected quite well in mixtures). For pyrovanadate, absorption bands at 710, 777, 832, 863, and 947 cm^{-1} are characteristic, and for hexavanadate at 906, 961, and 999-1010 cm^{-1}.

Thus, both methods confirmed the presence of broad homogeneity regions in uranyl vanadates. The preparation with $U : V = 3 : 2$ proved to be two-phase (pyrovanadate and α-$UO_2(OH)_2$). The composition $(UO_2)_3(VO_4)_2 \cdot 6H_2O$ is ascribed to the mineral ferganite (although recalculation of the analytical results gives the ratio $U : V = 2.5 : 2$). Apparently, the composition of ferganite requires clarification.

Anhydrous orthovanadate is obtained by heating the pyrovanadate with uranyl hydroxide to 575°. The melting point of $(UO_2)_3(VO_4)_2$, determined by the visual polythermal method, is 805-810° (simultaneously, decomposition of the orthovanadate into pyrovanadate and uranium uranous-uranic oxide occurs).

Dehydration of the pyrovanadate is accompanied by the formation of β-$(UO_2)_2V_2O_7$ (at 330°) and α-$(UO_2)_2V_2O_7$ (above 500°). The latter transition is apparently irreversible. The pyrovanadate melts at 790°.

* We use the terms "pyrovanadate" and "hexavanadate" because they reflect the composition of the preparations, although the corresponding ions may be absent in the structures of these compounds.

As a result of dehydration of the hexavanadate at 260°, β-$(\mathrm{UO_2})_2\mathrm{V_6O_{17}}$ is obtained, which then transforms into the α-modification (550°). Uranous uranate reacts with vanadium pentoxide at 460°; for the reaction to go to completion, heating to 550—650° is required. Depending on the ratios, orthovanadate (in the range 700—800°), pyrovanadate (α-modification), and hexavanadate (both modifications) may be formed. α-$(\mathrm{UO_2})_2\mathrm{V_6O_{17}}$ crystallizes in the orthorhombic system: $a = 10.40$; $b = 11.90$; $c = 5.69$ kX; $z = 2$; the most probable space group is $p222$.

Table 1

Values of the subcell periods of some oxygen compounds of uranium and vanadium

Compound	a, kX	c, kX	V, kX^3
$(\mathrm{UO_2})_2\mathrm{V_6O_{17}} \cdot n\mathrm{H_2O}$	3.46	–	–
β-$(\mathrm{UO_2})_2\mathrm{V_6O_{17}}$	3.461	4.17	44
$\mathrm{UV_3O_{10}}$	3.463	4.05	42.04
$\mathrm{UVO_5}$	3.561	4.123	46.6
$\mathrm{UV_2O_{6.1}}$	3.64	4.27	49

If vanadium pentoxide is heated in evacuated quartz ampoules with a mixture of uranium dioxide and uranous uranate of overall composition $\mathrm{U_2O_5}$, then at 600—1000° two new phases, $\mathrm{UV_3O_{10}}$ and $\mathrm{UVO_5}$, are formed. The solubility of uranium trioxide and uranous uranate in vanadium pentoxide is small (noticeably less than 10 mol. %).

Uranium tetraoxide apparently dissolves partially in uranium dioxide (about 0.5 mol. %). These two oxides form the compound UV_2O_6 (the reaction between UO_2 and V_2O_4 does not go to completion even after firing for 200 hr at 1000°). UV_2O_6 crystallizes in the trigonal system (structural type $PbSb_2O_6$): $a = 4.986 \pm 0.003$ kX, $c = 4.755 \pm 0.005$ kX, space group $p312$, $z = 1$; U in (a), V in (d) and (f) (confirmed by an intensity calculation). ThV_2O_6, synthesized under the same conditions, crystallizes in the tetragonal system (trirutile structural type) with $a = 5.046 \pm 0.005$; $c = 9.47 \pm 0.01$ kX; $z = 2$. V_2O_4 is practically insoluble in ThO_2. Vanadium trioxide does not react with uranium dioxide up to 2300° (somewhat above the melting temperature of the mixture). This is probably a system with a simple eutectic, as is also UO_2—Al_2O_3 (^{2}).

Among the products of reduction of uranium vanadates with hydrogen at 400 –900°, two new phases were found: $UV_2O_{6.1}$ and $UV_3O_{8.03}$ (the latter decomposes on firing into UO_{2+x} and V_2O_3). The final product of reduction is a mixture of uranium dioxide and vanadium trioxide. β-$(UO_2)_2V_6O_{17}$, UV_3O_{10}, UVO_5, $UV_2O_{6.1}$, and hydrous uranium hexavanadate form a group of compounds that are structurally close to one another. For β-$(UO_2)_2V_6O_{17}$ and UV_3O_{10}, crystals were obtained and were also studied by the Laue and rotation methods; the others were studied by the powder method. All compounds of this group have similar hexagonal subcells, in which the strong lines of the Debyegrams are indexed (Table 1).

In the case of anhydrous hexavanadate and UV_3O_{10}, true cells were found from rotation radiographs. In both cases the period a proved to be doubled, and c quadrupled. Such a superstructure may be explained by alternation of uranium and vanadium atoms at the nodes of the subcell. Each net of uranium and vanadium atoms in the $(hk0)$ plane will then retain hexagonal symmetry, but alternation of the layers must lead to the disappearance of third-order axes, and the cell becomes orthorhombic (space group $Fddd$) with the ratio $a/b = \sqrt{3}$. Uranium atoms must be located in (a), and vanadium in (b) and (g), with $z \approx 1/4$. Such an arrangement in the case of UV_3O_{10} is confirmed by calculation of the intensities of the Debyegram lines.

In the Debyegram of hydrous hexavanadate, only lines with indices $hk0$ are present, i.e., the structure of the hexavanadate is built of hexagonal nets formed by uranium and vanadium atoms, and it is impossible to identify a structural element corresponding to the anion, which makes it possible to regard the hexavanadate as a double hydroxide of uranium and vanadium. To an analogous con-

Makarov and Anikina arrived at this conclusion as a result of a structural study of umohoite, `UO_3 • MoO_3 • 4H_2O` (5).

In contrast to vanadium pentoxide, niobium pentoxide does not react with an aqueous suspension of uranyl hydroxide when heated for a week to a temperature of 100°. The preparation obtained under these conditions was a mixture of `$\alpha$-(UO_2)(OH)_2` and `Nb_2O_5`. On the heating curve there were endothermic effects due to removal of water (120 and 420°). As a result of dehydration, a mixture of `Nb_2O_5` and `$\gamma$-UO_3` is obtained. The endothermic effect at 675° corresponds to decomposition of uranium trioxide and formation of the uranous-uranic oxide. Above 1000° niobium pentoxide transforms into a high-temperature modification, which is also present in the calcination products at 1000-1100° together with the uranous-uranic oxide and `$\alpha$-Nb_2O_5`. As a result of reduction of the mixture `$\gamma$-UO_3` and `Nb_2O_5` with hydrogen at 800°, a mixture of `NbO_2` and `UO_2` is formed. Thus, under the conditions described, no compounds are formed between the oxides of uranium and niobium, despite the structural similarity of `$\alpha$-Nb_2O_5` to `U_3O_8` and `UO_3`. It is possible that the reaction between `Nb_2O_5` and `U_3O_8` proceeds at a higher temperature.

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