

Is Pure V_9O_{17} Unstable at 1268 K?

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Vasil'eva *et al.*¹ obtained high quality free energy of formation data for the $3 \leq n \leq 9$ members of the V_nO_{2n-1} series by an e.m.f. technique. The authors were unable to make a positive identification of V_9O_{17} by X-ray diffraction but reported indirect evidence for its thermodynamic stability. While their experimental results do indeed show very good agreement with this hypothesis, the stated experimental errors do not exclude the opposite interpretation.

Lower members of the series have been prepared from VO_2 at about 1270 K by the double buffer technique, which permits precise oxygen activity control. There was good agreement with the data of Vasil'eva *et al.* The results and the technique, with full experimental details, are being described elsewhere.²

In the present work, VO_2 was reduced by means of $CO + CO_2$ gaseous buffers using the same technique, with $Ni + NiO$ as the solid buffer. The products were examined by X-ray powder diffraction (Guinier-Hägg method). The experimental conditions and the results have been summarized in Table 1.

X-Ray diffraction work by Nagasawa³ revealed V_9O_{17} growing in a topotactic relationship with V_8O_{15} , while, in a high resolution electron microscopy study,⁴ Gannon and Tilley found V_9O_{17} primarily as microdomains coexisting with similar V_8O_{15} domains in a VO_2 parent phase. In both cases, the preparations were carried out at constant stoichiometry rather than at a controlled oxygen

activity, while some of the samples examined by Gannon and Tilley were clearly not in internal equilibrium. The present observations, however, prove V_8O_{15} to be the principal reaction product at 1268-9 K even under near-equilibrium conditions that would be expected to produce single phase V_9O_{17} or higher V_nO_{2n-1} series members. V_9O_{17} , on the other hand, was only found in the form of a few diffraction lines in a powder pattern from a sample that consisted mostly of V_8O_{15} . The existence of V_9O_{17} as a separate phase at this temperature is thus in some doubt.

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Table 1. Reduction of VO_2 with $CO + CO_2$ buffers.

$-\log p_{O_2}$ (p_{O_2} in atm)	T K	Reaction time h	Diffraction patterns found	Phases expected
6.70	1269	48	VO_2	VO_2 or V_nO_{2n-1} ($n > 9$)
6.94	1268	48	VO_2 (+ V_8O_{15})	VO_2 or V_nO_{2n-1} ($n > 9$)
7.12	1268	48	V_8O_{15} (+ $VO_2 + V_9O_{17}$)	VO_2 or V_nO_{2n-1} ($n > 9$)
7.19	1269	66	V_8O_{15}	V_9O_{17}