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Short Communication

Hydrothermal phase transformation of tungsten trioxide and the associated thermodynamic data

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Abstract

Hydrothermal phase stability studies of tungsten trioxide under water vapour pressure showed a monoclinic to tetragonal phase transformation with a nearly pressure independent invariant equilibrium boundary line. The standard thermodynamic data for the tetragonal form of WO_3 obtained from the experimental PT points on the equilibrium transformation boundary are:

$\Delta G^o_f = -759.743$ kJ/mol.,

$\Delta H^o_f = -836.598$ kJ/mol., $S^o_f = 82.59$ J/mol.deg.

Introduction

Hydrothermal stability studies on transition metal oxides have been of interest both from the point of view of synthesis of consistently stoichiometric stable oxide phases as well as retrieving the thermodynamic parameters for these oxides and hydroxide phases [1–4]. Tungsten trioxide is a stable phase which is usually associated with slight oxygen non-stoichiometry [5]. Besides, a number of polymorphic transformations with temperature at one atmosphere have been reported [6, 7]. At room temperature WO_3 is monoclinic and is stable up to 583 K, where it transforms to an orthorhombic structure. On further heating the orthorhombic form transforms to a tetragonal form at $\simeq 1010$ K [8]. The stability relations of tungsten trioxide at high temperature and pressure have not been studied hitherto, particularly under hydrothermal conditions. We report here the stability of WO_3 on the PT plane under hydrothermal conditions and the associated thermodynamic data for the phase transformations of WO_3 from the monoclinic to the tetragonal phase.

Results

Details of the experimental techniques have been described earlier [2, 9, 10]. The starting material was monoclinic WO_3 prepared by hydrothermally decomposing H_2WO_4 (from Wilson Laboratories, Analytical Reagent). The WO_3 prepared this way was found to be more reactive than the commercially available oxide. The starting charge was thus WO_3 and doubly distilled water sealed in platinum capsules. The experimental conditions of each run are given in Table 1. The equilibrium phase boundary for the monoclinic to tetragonal transformation on a PT plane is shown in Fig. 1. The solid products after the experiment were identified through X-ray powder diffractograms and comparisons withthe published ASTM cards (WO_3 monoclinic ASTM card No. 5.0363, WO_3 tetragonal ASTM card No. 5.0388). The monoclinic WO_3 in the product was found as a powdery greenish yellow material but tetragonal WO_3 formed dark steel blue coloured striated platelets. Some of these crystals show a sort of lamellar twinning. Scanning electron micrographs of the tetragonal crystals are shown in Fig. 2. Unlike in

TABLE 1. Experimental details of tungsten trioxide (m)–water system

Temperature °C	Pressure bars	Duration hrs.	Product
150	350	76	WO_3-m
450	350	86	WO_3-m
550	350	78	WO_3-m
650	350	96	WO_3-m
675	350	99	WO_3-m + t
700	350	116	WO_3-t
750	350	58	WO_3-t
800	700	88	WO_3-t
660	900	87	WO_3-m
700	900	79	WO_3-t
575	1100	84	WO_3-m
725	1150	59	WO_3-t
650	1450	77	WO_3-m
700	1450	64	WO_3-t
200	1750	84	WO_3-m
400	1750	59	WO_3-m
600	1750	66	WO_3-m
650	1750	64	WO_3-m
675	1750	69	WO_3-t
700	1750	85	WO_3-t
750	1750	63	WO_3-t

m = monoclinic, t = tetragonal

0254-0584/91/$3.50

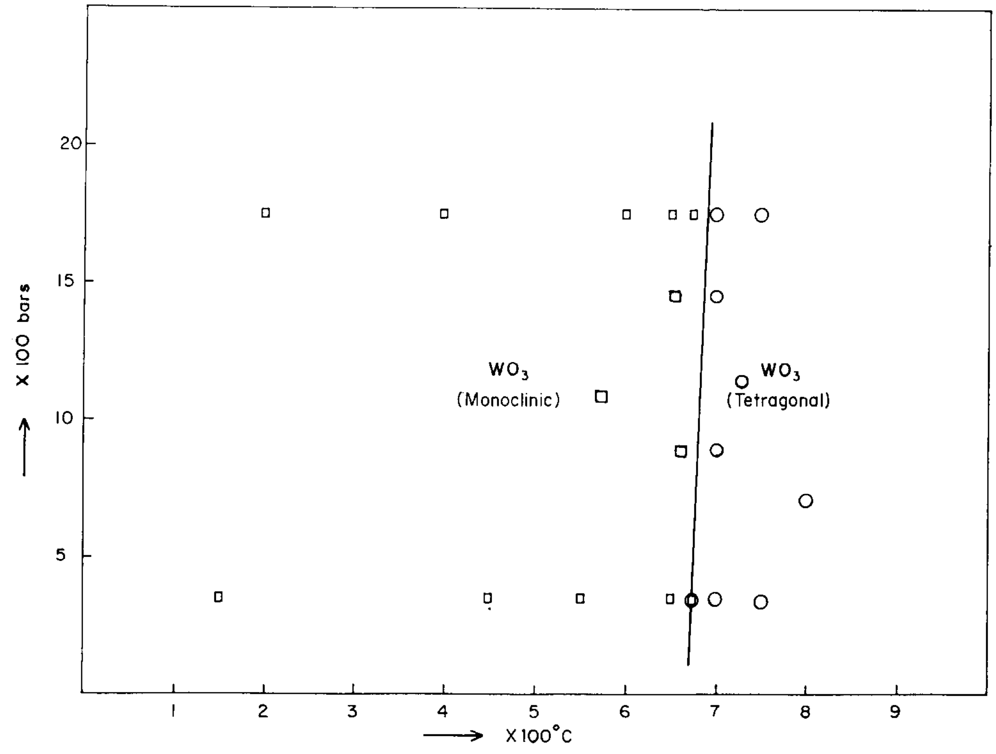

Fig. 1. Phase diagram for the $WO_{3(m)}$-H_2O system.

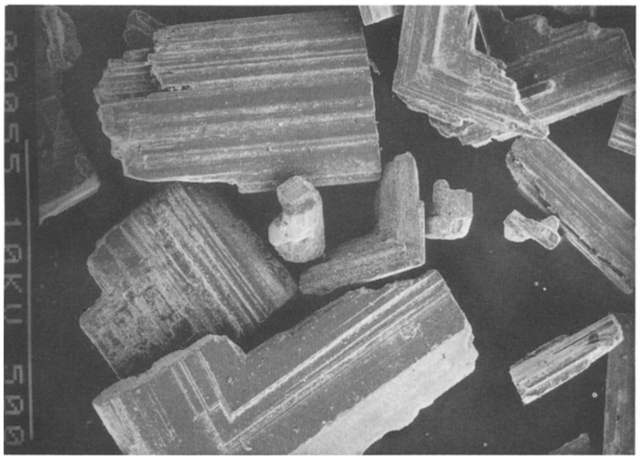

Fig. 2. Scanning electron micrograph of WO_3 (tetragonal) crystals, showing lamellar twinning.

high temperature transformations reported at 1 atmosphere [7, 11], we notice a direct change from monoclinic to tetragonal, skipping the orthorhombic phase which was found to appear as an intermediate between the monoclinic to tetragonal transformation. The phase transformation is almost pressure independent and the slope of this boundary line is 77.566 bars/K. The extrapolation of this phase transformation boundary line gives an equilibrium temperature of 944.6 K at 1 bar.

The volume change accompanying this phase transformation reaction is $\Delta V_r = V\ WO_3(t) - V\ WO_3(m)$, which is 0.84 cc. atm. The volume data for tetragonal and monoclinic forms of WO_3 were calculated from the unit cell data (monoclinic: $a_0 = 7.281$ Å; $b_0 = 7.52$ Å; $c_0 = 3.38$ Å; $\beta = \sin 91.5°$, tetragonal: $a_0 = 5.24$ Å; $c_0 = 3.92$ Å). The entropy of the reaction $\Delta S_{T,r} = 6.680$ J/mol.deg., at 944.6 K was found using the Clapeyron equation [$dP/dT = dS/dV$]. The accompanying enthalpy change $\Delta H_{T,r} = 6310.70$ J/mol., was estimated using the relation:

$$\Delta H_{T,r} = T.\Delta S_{T,r}.$$

Since the compounds involved in the reaction were only solids and that it was a phase transformation, one could safely consider the heat capacity change of reaction as zero. Therefore by Kirchoff's law $\Delta H_{T,r} = \Delta H_r^0$ and $\Delta S_{T,r} = \Delta S_r^0$. Standard free energy of reaction ΔG_r^0 is determined from the relationship:

$$\Delta G_r^0 = \Delta H_r^0 - T.\Delta S_r^0 = 4319.068 \text{ J/mol.}$$

From the reported values of the thermodynamic properties of monoclinic WO_3, it was possible to calculate the thermodynamic properties of the WO_3 tetragonal phase:

$\Delta G_f^0 = -759.743$ kJ/mol.,

$\Delta H_f^0 = -836.598$ kJ/mol., $S_f^0 = 82.59$ J/mol.deg.

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