

Thermochemistry of Ammonium Tungsten Bronze, $(\text{NH}_4)_{0.25}\text{WO}_3$

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The enthalpy of formation of ammonium tungsten bronze, $(\text{NH}_4)_{0.25}\text{WO}_3(\text{s})$, at 298.15 K has been determined by solution calorimetry. The value obtained for formation from $\text{NH}_3(\text{g})$, $\text{H}_2(\text{g})$ and $\text{WO}_3(\text{s})$ was $-25.7 \pm 0.8 \text{ k}^1 \text{ mol}^{-1}$. The stability of the bronze towards decomposition and oxidation is discussed.

Introduction

An ammonium tungsten bronze phase, $(\text{NH}_4)_x\text{WO}_3$, analogous to the hexagonal tungsten bronzes, M_xWO_3 , which are formed by the heavier alkali metals K, Rb, and Cs, can be prepared by the decomposition of ammonium paratungstate in hydrogen or ammonia (1, 2). The compound has also been synthesized hydrothermally from W metal, WO_3 and ammonium hydroxide solution at 700°C and 3,000 atm (3). The value of x in the formula $(\text{NH}_4)_x\text{WO}_3$ is dependent on the preparative conditions but usually lies in a fairly narrow range $0.25 \leq x \leq 0.33$. An upper limit on x is imposed crystallographically since in the hexagonal structure adopted ammonium ions reside in wide channels running parallel to the c -axis and a maximum occupancy of the channels occurs at $x = 0.33$ (4). In its electronic properties $(\text{NH}_4)_x\text{WO}_3$ behaves as a typical oxide bronze, showing metallic conductivity and weak temperature independent paramagnetism (2). Aspects of its thermochemistry have been explored qualitatively through thermogravimetric analysis (1, 2) and quantitative specific heat and entropy data for $(\text{NH}_4)_{0.25}\text{WO}_3$ have been obtained by Gannon (5).

The object of the present work was to obtain the enthalpy of formation of $(\text{NH}_4)_x\text{WO}_3$ at 298.15 K by means of solution calorimetry. Alkaline hexacyanoferrate (III) solution was used as reaction medium. No previous enthalpy of formation values exist for ammonium tungsten bronze.

Experimental

Materials

A sample of $(\text{NH}_4)_x\text{WO}_3$ was prepared by reduction of ammonium paratungstate, $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ in dry H_2 as described previously (2). Its formula was established (2) by chemical and thermogravimetric analysis to be $(\text{NH}_4)_{0.25 \pm 0.01}\text{WO}_3$. Examination by powder X-ray diffraction confirmed the presence of a pure hexagonal phase ($a = 7.388 \text{ \AA}$, $c = 7.551 \text{ \AA}$). Other materials used for calorimetry $\text{K}_3\text{Fe}(\text{CN})_6$, NH_4Cl and $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ were of B.D.H. analar grade. The reaction medium was a solution of 2g $\text{K}_3\text{Fe}(\text{CN})_6$ and 20g KOH in 100 ml water (vol at 20°C).

Heat of Formation Determination

Heats of reaction were measured with an LKB 8700 solution calorimeter operated at 298.15 K. A detailed description of the apparatus and its mode of operation have been given previously (6, 7); only an outline of the procedure followed is given here. An electrical calibration was made after each individual heat of reaction measurement. A solute charge of 0.100 g of $(\text{NH}_4)_{0.25}\text{WO}_3$ was used and the weights used of other reacting substances were approximately stoichiometric with it. 100 ml batches of the calorimetric reagent were used in all measurements. Reaction periods were of less than five minutes duration.

The calorimetric reactions used to obtain the enthalpy of formation of $(\text{NH}_4)_{0.25}\text{WO}_3$ are given in skeleton form in Table I, together with average measured enthalpy changes and their

TABLE I
CALORIMETRIC REACTION SCHEME FOR $(\text{NH}_4)_{0.25}\text{WO}_3$

Reaction	$\Delta H_{298.15\text{K}}/\text{kJ}$
(1) $(\text{NH}_4)_{0.25}\text{WO}_3(\text{s}) + 0.25\text{Fe}(\text{CN})_6^{3-}(\text{sol}) + 2.25\text{OH}^-(\text{sol})$ $= \text{H}_2\text{O}(\text{sol}) + 0.25\text{NH}_4\text{OH}(\text{sol}) + \text{WO}_4^{2-}(\text{sol}) + 0.25\text{Fe}(\text{CN})_6^{4-}(\text{sol})$	-84.7 ± 0.3 (3)
(2) $\text{K}_3\text{Fe}(\text{CN})_6(\text{s}) = 3\text{K}^+(\text{sol}) + \text{Fe}(\text{CN})_6^{4-}(\text{sol})$	$+43.7 \pm 0.5$ (3)
(3) $\text{KCl}(\text{s}) = \text{K}^+(\text{sol}) + \text{Cl}^-(\text{sol})$	$+14.9 \pm 0.04$ (3)
(4) $3\text{H}_2\text{O}(\text{l}) = 3\text{H}_2\text{O}(\text{sol})$	-0.17 ± 0.01 (4)
(5) $\text{WO}_3(\text{s}) + 2\text{OH}^-(\text{sol}) = \text{WO}_4^{2-}(\text{sol}) + \text{H}_2\text{O}(\text{sol})$	-61.9 ± 0.5 (6)
(6) $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}(\text{s}) = 4\text{K}^+(\text{sol}) + \text{Fe}(\text{CN})_6^{4-}(\text{sol}) + 3\text{H}_2\text{O}(\text{sol})$	$+46.2 \pm 0.3$ (3)
(7) $\text{NH}_4\text{Cl}(\text{s}) + \text{OH}^-(\text{sol}) = \text{NH}_4\text{OH}(\text{sol}) + \text{Cl}^-(\text{sol})$	$+7.9 \pm 0.2$ (3)
(8) $(\text{NH}_4)_{0.25}\text{WO}_3(\text{s}) + 0.25\text{K}_3\text{Fe}(\text{CN})_6(\text{s}) + 0.25\text{KCl}(\text{s}) + 0.75\text{H}_2\text{O}(\text{l})$ $= \text{WO}_3(\text{s}) + 0.25\text{NH}_4\text{Cl}(\text{s}) + 0.25\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}(\text{s})$ $\Delta H_8 = \Delta H_1 + 0.25(\Delta H_2 + \Delta H_3 + \Delta H_4) - \Delta H_5 - 0.25(\Delta H_6 + \Delta H_7)$ $= -21.7 \pm 0.6$ kJ at 298.15 K.	

uncertainties. The number of determinations made of each calorimetric heat of solution is given in parentheses. The uncertainties given for individual heats of solution are twice the standard error of the mean and the overall uncertainty quoted for a thermochemical cycle is the root of the sum of the squares of the individual uncertainties. The symbols (s) and (l) designate solid and liquid substances respectively and the symbol (sol) indicates that the number of mols of substance shown in Table I was dissolved in reagent of molar composition [$14.33\text{K}_3\text{Fe}(\text{CN})_6$, 841.3KOH , $13\text{H}_2\text{O}$].

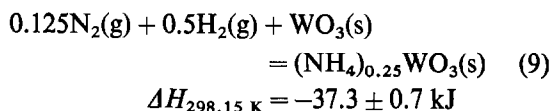
Reactions (1), (4) and (7) were measured directly in the present work. Reactions (2), (3), (5) and (6) had been measured previously by the authors under identical conditions (6, 8). Three measurements of reaction (1) were made, -85.0 , -84.4 , -84.7 kJ mol⁻¹. Reaction (4) was a dilution reaction required to maintain stoichiometry in the reaction scheme. Three measurements of the heat gave, -0.17 , -0.17 , -0.18 kJ for 3 mols H₂O. Three measurements of the heat of reaction (7) gave $+7.7$, $+8.0$, $+8.0$ kJ mol⁻¹.

Reaction (8) represents the overall calorimetric process, the reaction actually measured in the present work. The enthalpy change of the reaction at 298.15 K is obtained by summation of the heats of reaction (1)–(7) as specified in Table I.

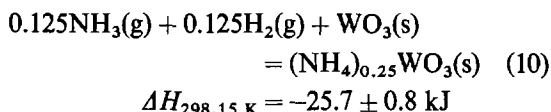
The standard enthalpies of formation of the remaining compounds listed in eqn (8) must be known in order to obtain the enthalpy of formation of $(\text{NH}_4)_{0.25}\text{WO}_3$ (at 298.15 K). The values taken were (kJ mol⁻¹) $\text{K}_3\text{Fe}(\text{CN})_6(\text{s})$, -242.7 ± 0.5

(9, 10, 11), $\text{KCl}(\text{s})$, -436.0 ± 0.8 (12), $\text{H}_2\text{O}(\text{l})$, -285.85 ± 0.04 (12), $\text{NH}_4\text{Cl}(\text{s})$, -314.4 ± 0.5 (10), $\text{NH}_3(\text{g})$, -46.6 ± 1.0 (10), $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}(\text{s})$, -1458.1 ± 0.5 , (9, 10, 11, 12).

Combination of the measured enthalpy change for reaction (8) with the standard data gave as final result:



The corresponding value for the enthalpy of formation from $\text{NH}_3(\text{g})$, $\text{H}_2(\text{g})$ and $\text{WO}_3(\text{s})$ is:

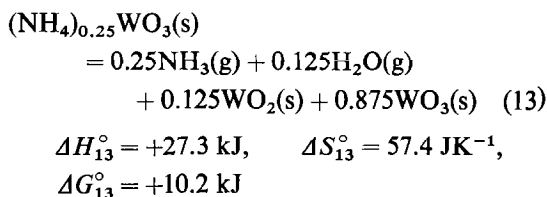
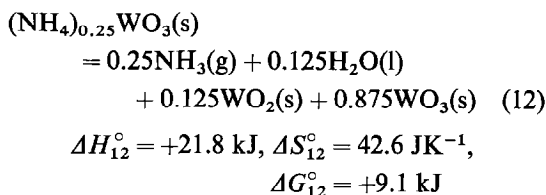
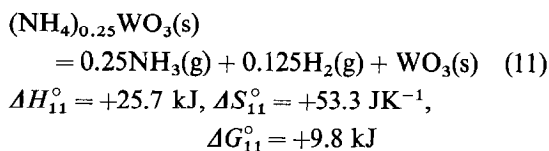
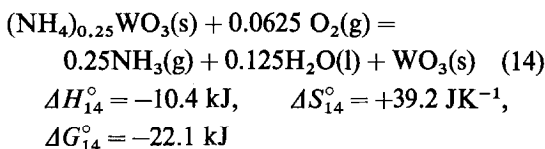


Discussion

The measured enthalpy of formation and entropy (5) of $(\text{NH}_4)_{0.25}\text{WO}_3$ can be combined with the standard thermodynamic data (10, 12) listed below to determine the thermodynamic stability of the ammonium tungsten bronze phase towards decomposition and oxidation.

Substance	$(\text{NH}_4)_{0.25}\text{WO}_3$	$\text{WO}_3(\text{s})$	$\text{WO}_2(\text{s})$	$\text{H}_2\text{O}(\text{l})$
$\Delta H_{f298.15\text{K}}/\text{kJmol}^{-1}$	-880.0	-842.7	-589.5	-285.8
$S_{298.15\text{K}}^0/\text{JK}^{-1}\text{mol}^{-1}$	86.96	75.90	50.54	69.64
Substance	$\text{H}_2\text{O}(\text{g})$	$\text{H}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{NH}_3(\text{g})$
$\Delta H_{f298.15\text{K}}/\text{kJmol}^{-1}$	-241.8	—	—	-46.6
$S_{298.15\text{K}}^0/\text{JK}^{-1}\text{mol}^{-1}$	188.7	130.58	205.02	192.3

Calculated values of relevant thermodynamic functions at 298.15 K are as follows:

Decomposition*Oxidation*

Reactions (11) and (12) represent alternative modes of decomposition of the ammonium bronze in the absence of oxygen. Reaction (13) is a modification of (12), which becomes relevant at elevated temperatures when H₂O is a vapor. Reaction (14) is the oxidation of the bronze.

It is apparent that (NH₄)_{0.25}WO₃(s) is thermodynamically stable to decomposition in the absence of oxygen but becomes metastable in its presence. At elevated temperatures the decomposition products in the absence of oxygen contain lower oxides of tungsten (1, 2). An approximate decomposition temperature for reaction (13) can be calculated from $T_{\text{decomp}} \sim \Delta H_{13}^\circ / \Delta S_{13}^\circ$

= 475 K. In fact, vacuum decomposition does not occur to any appreciable extent below 650 K, and it must be concluded that the decomposition process is kinetically controlled. Similarly although the ammonium bronze is thermodynamically unstable to oxidation at room temperature, the rate of oxidation of the bronze on exposure to air is found to be negligible. Again kinetic factors control the process. An interesting contrast in behavior in this respect is provided by the analogous hydrogen tungsten bronze, H_xWO₃, where at room temperature oxidation occurs rapidly in the air, in agreement with the measured thermodynamics (8).

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