Thermochemistry of Hydrogen Tungsten Bronze Phases H_xWO_3

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The enthalpies of formation of two hydrogen tungsten bronze phases $H_{0.35}WO_3$ and $H_{0.18}WO_3$ have been determined by solution calorimetry. Values obtained for formation from $H_2(g)$ and $WO_3(s)$ at 298.15 K were $H_{0.35}WO_3(s)$, -9.6 ± 0.8 kJ mole^{-1} and $H_{0.18}WO_3(s)$, -4.8 ± 0.6 kJ mole^{-1}. The stabilities of these phases towards decomposition, disproportionation and oxidation are discussed.

Introduction

The first detailed account of the preparation of hydrogen tungsten bronze phases H_xWO_3 ($0 < x < 0.6$) by reduction of WO_3 with active hydrogen was given by Glemser and Naumann (*1*). The phases so formed resemble the sodium tungsten bronzes, Na_xWO_3, both electronically and structurally and can be regarded as "oxide bronzes" (*2, 3*). Three distinct phases are found (*2, 3*); tetragonal B ($0.15 < x < 0.23$) tetragonal A ($0.33 < x < 0.5$) and cubic ($x > 0.5$). Crystalline hydrogen tungsten bronze samples are stable *in vacuo* to >400 K, but are unstable in air with respect to oxidation. They are soluble in alkaline potassium hexacyanoferrate (III) solution at 25°C. A recent structural study by Wiseman and Dickens (*4*) has established the cubic phase as a nonstoichiometric oxide hydroxide, $WO_{3-n}(OH)_n$; each hydrogen atom is attached to oxygen by an –OH bond and the W–O framework constitutes a distorted ReO_3-type lattice. No quantitative enthalpy data were available for these phases and the object of the present work was to determine enthalpies of formation by means of solution calorimetry.

Experimental

Materials

Polycrystalline samples of hydrogen tungsten bronze, of composition $H_{0.35}WO_3$, were prepared from B.D.H. analar grade WO_3 by reduction with zinc and boiling dilute HCl over a period of 6 hr. Excess zinc was removed by prolonged boiling with additional HCl solution and subsequent washings with water. Samples were dried in a vacuum desiccator and sealed in pyrex tubes under vacuum. A sample of composition $H_{0.18}WO_3$ was prepared from $H_{0.35}WO_3$ by quantitative oxidation with pure oxygen at 100°C in a sealed tube (24 hr).

The hydrogen contents of the products were determined by decomposition at 400°C to give a measured pressure of hydrogen gas in a known volume (water vapor being frozen out).

$$H_xWO_3(s) = pH_2(g) + mH_2O(s) + WO_{3-m}(s)$$
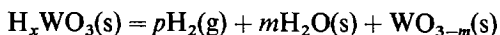
The composition of the reduced oxide WO_{3-m} was determined by thermogravimetric oxidation at 650°C to WO_3. Knowledge of p and m enabled x to be calculated with an estimated error of ± 0.005.

Examination by X-ray diffractometry and comparison with the data of Refs. *2* and *3* showed that $H_{0.18}WO_3$ was a pure tetragonal B phase and $H_{0.35}WO_3$ was pure tetragonal A.

High surface area tungstic oxide, WO_3 (HA) was prepared by heating tungstic acid, H_2WO_4, (Koch-Light) at 250°C in the absence of light and reducing agents (*5*). Thermogravimetric analysis established a purity of 99.87% for the sample. The B.E.T. surface area, determined by krypton adsorption at 77 K was 22.7 ± 0.2 m^2 g^{-1}. Hydrochloric acid solution for calorimetry, was prepared by dilution of B.D.H. analar grade HCl solution to the composition [HCl, 179.805 H_2O], as determined by titration against borax.

Other materials used for calorimetry, $K_3Fe(CN)_6$. KCl and $K_4Fe(CN)_6 \cdot 3H_2O$, were of B.D.H, analar grade. KCl and $K_3Fe(CN)_6$ were dried at 100°C and kept in a vacuum desiccator before use. The specific surface area of B.D.H. tungstic oxide, WO_3 (LA) was determined as 7.5 ± 0.3 $m^2 g^{-1}$ and the hydrogen tungsten bronze phases made from this material remained substantially unchanged in particle size. The reaction medium was a solution of 2 g $K_3Fe(CN)_6$ and 20 g KOH in 100 ml water.

Heat of Formation Determinations

Heats of reaction were measured with an LKB 8700 constant environment solution calorimeter operated at 298.15 K and 323.15 K. A detailed description of this standard commercial instrument and its operation has been given previously, (*6, 12*), and only an outline of the procedure followed is given here. An electrical calibration experiment was made in conjunction with each individual heat of reaction measurement. One-hundred-milliliter batches of the calorimetric solvent were used in all measurements. A solute charge of 0.1 g (0.43 m mole) of H_xWO_3 was used, and the charges taken of other reactants were stoichiometric with this in accordance with the reaction scheme given in Table I. Reaction periods were of less than ten-minutes duration in all cases. The calorimetric reactions used for obtaining the enthalpies of

formation of H_xWO_3 are given in skeleton form in Table I, together with the average measured heats of reaction and their uncertainties. The number of determinations 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) are used to designate solid and liquid substances respectively and the symbol (sol) indicates that the number of moles of substance shown in Table I was dissolved in reagent of composition [14.08 $K_3Fe(CN)_6$, 826.4 KOH, 12870 H_2O].

Reactions (1)–(7) were conducted independently into separate batches of solvent. Reaction (6) for WO_3 (HA) was also conducted consecutively with Reaction (5); no difference could be observed between the heat of Reaction (6) measured independently and measurement of the same reaction made consecutively with Reaction (5).

Five measurements of Reaction (1) were made for each bronze sample; the results for $H_{0.18}WO_3$ were: -86.8, -87.0, -86.7, -86.4, and -86.6 kJ $mole^{-1}$ and for $H_{0.35}WO_3$: -109.8, -110.5, -109.9, -110.3, and -110.1 kJ $mole^{-1}$.

Three measurements of the heat of Reaction (2) gave $+44.2$, $+43.6$, $+43.4$ kJ $mole^{-1}$. Reaction (3) was a dilution reaction required to maintain stoichiometry in the reaction scheme. Six

TABLE I

CALORIMETRIC REACTION SCHEME FOR H_xWO_3

Reaction	$\Delta H_{298.15 \text{ K}}/kJ$			
	$x = 0.18$		$x = 0.35$	
(1) $H_xWO_3(s) + (2 + x)OH^-(sol) + xFe(CN)_6^{3-}(sol) =$				
$\quad (1 + x)H_2O(sol) + WO_4^{2-}(sol) + xFe(CN)_6^{4-}(sol)$	-86.7 ± 0.2	(*5*)	-110.1 ± 0.3	(*5*)
(2) $xK_3Fe(CN)_6(s) = 3xK^+(sol) + xFe(CN)_6^{3-}(sol)$	$+7.9 \pm 0.1$	(*3*)	$+15.3 \pm 0.2$	(*3*)
(3) $182.805x\ H_2O(l) = 182.805x\ H_2O(sol)$	-2.45 ± 0.03	(*6*)	-4.77 ± 0.05	(*6*)
(4) $xKCl(s) = xK^+(sol) + xCl^-(sol)$	$+2.7 \pm 0.01$	(*3*)	$+5.2 \pm 0.01$	(*3*)
(5) $xK_4Fe(CN)_6 \cdot 3H_2O(s) =$				
$\quad 4xK^+(sol) + xFe(CN)_6^{4-}(sol) + 3xH_2O(sol)$	$+8.4 \pm 0.05$	(*3*)	$+16.2 \pm 0.1$	(*3*)
(6) $WO_3(s) + 2OH^-(sol) = WO_4^{2-}(sol) + H_2O(sol)$	-61.9 ± 0.5		-61.9 ± 0.5	
(7) $x[HCl, 179.805\ H_2O](l) + xOH^-(sol) =$				
$\quad xH_2O(sol) + xCl^-(sol) + 179.805\ xH_2O(sol)$	-14.12 ± 0.04	(*4*)	-27.46 ± 0.07	(*4*)
(8) $H_xWO_3(s) + xK_3Fe(CN)_6(s) + 182.805x\ H_2O(l) + xKCl(s) =$				
$\quad WO_3(s) + xK_4Fe(CN)_6 \cdot 3H_2O(s) + x[HCl, 179.805\ H_2O](l)$	-11.0 ± 0.55		-21.2 ± 0.63	
$\quad \Delta H_8 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_5 - \Delta H_6 - \Delta H_7$				

measurements of the heat gave -13.36, -13.69, -13.78, -13.66, -13.45, and -13.77 kJ per 182.805 mole of H_2O. Three measurements of the heat of Reaction (4) gave $+14.9$, $+14.9$, $+14.9$ kJ mole^{-1}. Three measurements of the heat of Reaction (5) gave $+46.0$, $+46.5$, and $+46.0$ kJ mole^{-1}.
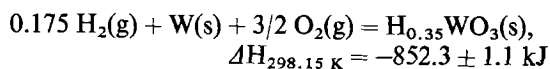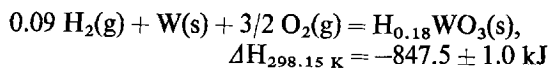
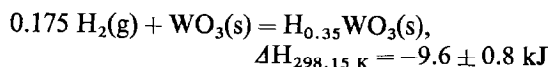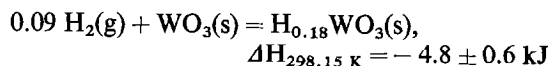Direct measurement of the heat of Reaction (6) at 25°C was not possible using WO_3 (LA), that is with material of the same particle size as the hydrogen tungsten bronze samples, since solution was incomplete at this temperature. ΔH_6 (298.15 K) was estimated indirectly as follows. High surface area tungstic oxide, WO_3 (HA), which dissolved readily at 25°C, was used with resulting heat measurements of -65.7, -66.2, -65.5, -65.9, -65.6 kJ mole^{-1} (mean value, -65.8 kJ mole^{-1}). The same material was used for heat determinations at 50°C with the following results, -63.5, -62.4, -62.8, -62.9, -62.7, -63.1 kJ mole^{-1} (mean value -62.9 kJ mole^{-1}).

The difference between measured heats of solution of WO_3 (HA) at 25° and 50°C is thus 2.9 kJ mole^{-1}. Low area tungstic oxide, WO_3 (LA) dissolved in less than five minutes in the calorimetric reagent at 50°C with resulting heat determinations of -58.9, -58.6, -59.0, -59.3, -58.7, -59.3 kJ mole^{-1} (mean value -59.0 kJ mole^{-1}). A value of the corresponding heat of solution of 25°C for WO_3 (LA) was estimated by subtracting 2.9 kJ mole^{-1} from the mean value obtained at 50°C, to give a final result for ΔH_6(298.15 K) $= -61.9 \pm 0.5$ kJ mole^{-1}. Reaction (7) was required to maintain stoichiometry in the calorimetric reaction scheme. Four heat measurements were made with the results, -78.60, -78.18, -78.40, and -78.46 kJ mole^{-1} of HCl in solution of composition [HCl, 179.805 H_2O].

Reaction (8) represents the overall calorimetric process, the reaction actually measured in the present work. The enthalpy change of this reaction at 298.15 K is obtained by summation of the heats of Reactions (1)–(7) as specified in Table I. To obtain the enthalpies of formation of the hydrogen tungsten bronze phases use is made of the following standard enthalpies of formation (kJ mole^{-1}): $K_3Fe(CN)_6$(s), -242.7 ± 0.5 (7–9), KCl(s), -436.0 ± 0.8 (10), H_2O(l), -285.85 ± 0.04 (10), $K_4Fe(CN_6 \cdot 3H_2O$(s), -1458.1 ± 0.5 (7–10), [HCl, 179.805 H_2O](l), -166.33 ± 0.10 (8),[1] WO_3(s), -842.7 ± 0.8 (10).

[1] Enthalpy of formation from H_2(g), Cl_2(g) and H_2O(l).
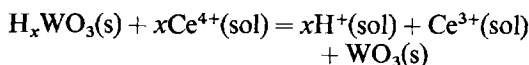
Combination of the measured enthalpies for Reaction (8) with the standard data given above yields the final results:

$$0.09\ H_2(g) + WO_3(s) = H_{0.18}WO_3(s),$$
$$\Delta H_{298.15\ K} = -4.8 \pm 0.6\ kJ$$

$$0.175\ H_2(g) + WO_3(s) = H_{0.35}WO_3(s),$$
$$\Delta H_{298.15\ K} = -9.6 \pm 0.8\ kJ$$

$$0.09\ H_2(g) + W(s) + 3/2\ O_2(g) = H_{0.18}WO_3(s),$$
$$\Delta H_{298.15\ K} = -847.5 \pm 1.0\ kJ$$

$$0.175\ H_2(g) + W(s) + 3/2\ O_2(g) = H_{0.35}WO_3(s),$$
$$\Delta H_{298.15\ K} = -852.3 \pm 1.1\ kJ$$

Discussion

Enthalpies of Formation of H_xWO_3

The enthalpies of formation determined in this work were obtained using complete solution processes. Previously, Neild (6) had used ceric sulphate in acid solution as calorimetric reagent to measure the heat of reaction (at 50°C) for:

$$H_xWO_3(s) + xCe^{4+}(sol) = xH^+(sol) + Ce^{3+}(sol) + WO_3(s)$$

a process which leaves WO_3(s) in suspension as an insoluble reaction product. Combination of the measured heats for this reaction with standard heat data for Ce^{4+}/Ce^{3+} (at 25°C) led to estimates for the enthalpies of formation from H_2(g) and WO_3(s) of two H_xWO_3(s) phases, $H_{0.38}WO_3$(s) (tetragonal A), -12.8 ± 3.7 kJ mole^{-1}, and $H_{0.16}WO_3$(s) (tetragonal B), -4.5 ± 1.7 kJ mole^{-1} at 298.15 K. Although the experimental precision is low, these values provide confirmation, via an independent thermochemical cycle, of the new and more precise enthalpy data obtained in the present work, namely $H_{0.35}WO_3$(s) (tetragonal A), -9.6 ± 0.8 kJ mole^{-1} and $H_{0.18}WO_3$(s) (tetragonal B), -4.8 ± 0.6 kJ mole^{-1}. From these last values the corresponding integral molar enthalpies of solution of H_2(g) into WO_3(s) to form tetragonal A and B phases of H_xWO_3(s) are -27.4 ± 2.3 kJ and -26.7 ± 3.3 kJ per mole of atomic hydrogen, respectively. A significant difference between the binding energies of hydrogen in the two phases was not found.

Thermodynamic Stability of H_xWO_3

The thermodynamic stability of H_xWO_3 towards decomposition, disproportionation and oxidation can be evaluated using the measured enthalpies of formation, the measured entropy
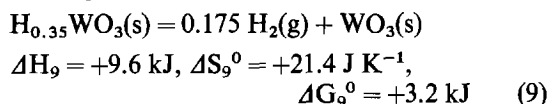
of $H_{0.40}WO_3(s)$ (11) and the standard thermo-dynamic data given below (8, 10):

Vacuum decomposition of crystalline samples of H_xWO_3 revealed a broad decomposition region

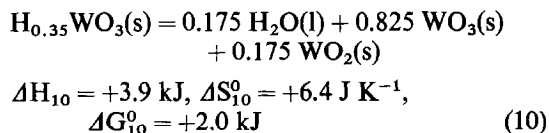| Substance	$WO_3(s)$	$WO_2(s)$	$H_2O(l)$	$H_2(g)$	$O_2(g)$
$\Delta H_f^0{}_{298.15\,K}$/kJ mole^{-1}	−842.7	−589.5	−285.8		
$S^0_{298.15\,K}$/J K^{-1} mole^{-1}	75.90	50.54	69.94	130.58	205.02

Gannon (11) obtained $S^0_{298.15\,K}H_{0.40}WO_3(s) =$ 77.53 J K^{-1} mole^{-1}. An interpolation between this value and the value given above for $S_{298.15\,K}WO_3(s)$ gives $S^0_{298.15\,K}H_{0.35}WO_3(s)$ ~77.33 J K^{-1} mole^{-1}.

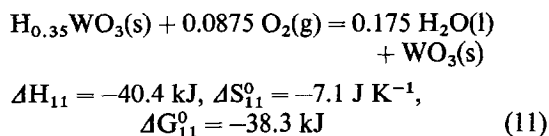Values of thermodynamic functions at 298.15 K have been calculated accordingly:

Decomposition:

$H_{0.35}WO_3(s) = 0.175\ H_2(g) + WO_3(s)$

$\Delta H_9 = +9.6\ kJ, \Delta S_9^0 = +21.4\ J\ K^{-1},$
$$\Delta G_9^0 = +3.2\ kJ \qquad (9)$$

Disproportionation

$H_{0.35}WO_3(s) = 0.175\ H_2O(l) + 0.825\ WO_3(s)$
$$+ 0.175\ WO_2(s)$$

$\Delta H_{10} = +3.9\ kJ, \Delta S_{10}^0 = +6.4\ J\ K^{-1},$
$$\Delta G_{10}^0 = +2.0\ kJ \qquad (10)$$

Oxidation:

$H_{0.35}WO_3(s) + 0.0875\ O_2(g) = 0.175\ H_2O(l)$
$$+ WO_3(s)$$

$\Delta H_{11} = -40.4\ kJ, \Delta S_{11}^0 = -7.1\ J\ K^{-1},$
$$\Delta G_{11}^0 = -38.3\ kJ \qquad (11)$$

It can be concluded that at 298.15 K $H_{0.35}WO_3$ (and $H_{0.16}WO_3$) is marginally stable towards decomposition to $H_2(g)$ and $WO_3(s)$, and also towards disproportionation to $H_2O(l)$ and lower oxides of tungsten. However, even at room temperature H_xWO_3 phases are thermodynamic-ally very unstable towards oxidation, as is observed experimentally. An approximate de-composition temperature for $H_{0.35}WO_3$ can be calculated for Eq. (9) by writing

$$T_{decomp} \sim \Delta H_9/\Delta S_9^0 = 449\ K.$$

over the range 470–670 K suggesting that under these conditions the decomposition is kinetically rather than thermodynamically controlled. Both H_2 and H_2O were formed as gaseous products establishing that decomposition and dispropor-tionation proceed simultaneously at elevated temperatures.

Acknowledgment

References

1. O. GLEMSER AND C. NAUMANN, Z. Anorg. Allg. Chem. **265**, 289 (1951).
2. P. G. DICKENS AND R. J. HURDITCH, Nature (London) **215**, 1266 (1967).
3. P. G. DICKENS AND R. J. HURDITCH, in "The Chemistry of Extended Defects in Nonmetallic Solids" (L. Eyring and M. O'Keefe, Eds.), p. 555, North Holland, Amsterdam (1970).
4. P. J. WISEMAN AND P. G. DICKENS, J. Solid State Chem. **6**, 374 (1973).
5. V. I. SPITSYN AND N. N. PATSUOKOVA, Russ. J. Inorg. Chem. **10** (2), 1304 (1965).
6. D. J. NEILD, Ph.D. Thesis, Oxford (1970).
7. P. A. ROCK, J. Phys. Chem. **70**, 576 (1966).
8. National Bureau of Standards, Circular 500 (1952) and Technical Notes 270 (1–4) (1968–69).
9. L. G. HEPLER, J. R. SWEET, AND R. A. JESSER, J. Amer. Chem. Soc. **82**, 304 (1960).
10. O. KUBASCHEWSKI, E. L. EVANS, AND C. B. ALCOCK, "Metallurgical Thermochemistry," 4th ed., Pergamon, New York (1967).
11. D. GANNON, Ph.D. Thesis, London (1970).
12. I. WADSÖ, Sci. Tools **13**, 33 (1966).