Thermochemistry of the Mixed Molybdenum Tungsten Oxides, $Mo_yW_{1-y}O_3$ (0.25 ≤ y ≤ 0.69), and Their Hydrogen Insertion Compounds, $H_xMo_yW_{1-y}O_3$ (0.34 ≤ x ≤ 0.98)

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The enthalpies of formation of a series of mixed metal oxides, $Mo_yW_{1-y}O_3$ (y = 0.25, 0.5, 0.64, and 0.69), and hydrogen insertion compounds, $H_{0.54}Mo_{0.25}W_{0.75}O_3$, $H_xMo_{0.5}W_{0.5}O_3$ (x = 0.63 and 0.66) and $H_xMo_{0.69}W_{0.31}O_3$ (x = 0.34, 0.45, and 0.98) have been determined by solution calorimetry. The enthalpies of hydrogen insertion into the mixed oxides are compared to those for the simple oxides MoO_3 and WO_3, which have been recalculated. The stability of the insertion compounds toward oxidation is discussed. © 1986 Academic Press, Inc.

Introduction

Tungsten trioxide has a monoclinically distorted ReO_3-like structure formed from corner-sharing octahedra, whereas molybdenum trioxide adopts a unique layer structure. The phases formed by the mixed oxides $Mo_yW_{1-y}O_3$ have been investigated by Salje (*1*) and shown to form WO_3-like structures for y ≤ 0.97.

The hydrogen insertion compounds $H_x Mo_yW_{1-y}O_3$ (x < 1.13, 0.1 < y < 0.9), previously characterized by the authors (*2*), also closely resemble those formed by WO_3 (*3*). A tetragonal phase ~0.1 < x < ~0.2 and a cubic phase 0.35 < x are formed in which the metal oxide framework is retained. The hydrogen uptake of the mixed molybdenum tungsten oxides is greater than in WO_3, since Mo(VI) is more readily reduced than

W(VI). Under standard conditions (1 atm H_2 25°C) the maximum hydrogen content is equal to $1.24y + 0.36(1 - y)$ for both the mixed oxides and WO_3. The phases formed by H_xMoO_3 (*4*) have layer structures and are stable with respect to hydrogen evolution with x < 1.7.

Thermochemical studies of the insertion compounds H_xWO_3 and H_xMoO_3 have been published (*5, 6*). The aim of the present work was to determine the enthalpies of formation of a number of mixed oxides $Mo_y W_{1-y}O_3$ and of the corresponding hydrogen insertion compounds $H_xMo_yW_{1-y}O_3$.

Experimental Materials

The preparation and characterisation of the mixed oxides $Mo_yW_{1-y}O_3$ and the hydrogen insertion compounds has been described previously (*2*). An additional oxide sample was prepared by removing un-

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reacted MoO_3 from the product of a sealed tube preparation, with MoO_3/WO_3 in a $4:1$ ratio, using ammonium hydroxide. This gave a sample of the zeta phase mixed oxide with the composition $Mo_{0.64}W_{0.36}O_3$.

The following oxide samples were used. The phases were identified by comparison with the X-ray data of Salje (*1*):

$Mo_{0.25}W_{0.75}O_3$ (γ), $Mo_{0.5}W_{0.5}O_3$ (ζ),

$Mo_{0.64}W_{0.36}O_3$ (ζ), and $Mo_{0.69}W_{0.31}O_3$

(predominantly θ).

Small amounts of other phases were found in the last sample, but X-ray microanalysis showed the molybdenum : tungsten ratio of different crystallites not to differ by more than $\pm 3\%$.

All the hydrogen insertion compounds $H_x Mo_y W_{1-y} O_3$ studied belonged to the cubic phase. The compounds used and the individual methods of preparation were

Sample	Preparation
$H_{0.34}Mo_{0.69}W_{0.31}O_3$	H_2/Pt
$H_{0.45}Mo_{0.69}W_{0.31}O_3$	Zn/HCl
$H_{0.98}Mo_{0.69}W_{0.31}O_3$	H_2/Pt
$H_{0.63}Mo_{0.5}W_{0.5}O_3$	Zn/HCl
$H_{0.66}Mo_{0.5}W_{0.5}O_3$	Zn/HCl
$H_{0.54}Mo_{0.25}W_{0.75}O_3$	H_2/Pt

The reaction medium for calorimetry consisted of 40 g $K_3Fe(CN)_6$ dissolved in 1.99 dm^3 of 3.05 ± 0.05 M KOH solution.

The air-sensitive hydrogen insertion compounds were loaded into calorimeter ampoules under dry nitrogen.

Determination of Enthalpies of Formation

Enthalpies of reaction (at 298.15 and 323.15 K) were measured using an LKB 8700 isoperibolic calorimeter. The instrument and mode of operation have been described previously (*7*). Sample charges of 25–110 mg were dissolved in 100-cm^3 batches of the calorimetric reagent. No discernible change in the enthalpies of reaction occurred on varying the sample mass, and previous work has also shown that, for a large excess of reagent, consecutive addition and the maintenance of strict stoichiometry for the components on both sides of the reaction is unnecessary. Fresh aliquots of reaction medium were therefore used for each experiment. At least four enthalpy of reaction measurements were made on each sample, and the uncertainty quoted in the mean is twice the standard error of the mean. Detailed calorimetric data for all the samples have been tabulated (*8*).

The Mixed Oxides

$Mo_{0.69}W_{0.31}O_3$ reacted rapidly at 298.15 K. The other oxides had to be studied at 323.15 K, since they reacted only slowly at

TABLE I

CALORIMETRIC REACTION SCHEME FOR $Mo_yW_{1-y}O_3$

| Reaction	y	$\Delta H_{298.15\ K}$ (kJ mole^{-1})	$\Delta H_{323.15\ K}$ (kJ mole^{-1})
(1) $Mo_yW_{1-y}O_3(s) + 2OH^-(sol) = y[MoO_4]^{2-}(sol)$	0.69	-79.10 ± 0.32	
$+ (1-y)[WO_4]^{2-}(sol) + H_2O(sol)$	0.64		-74.09 ± 0.82
	0.50		-70.53 ± 0.27
	0.25		-66.51 ± 0.14
(2) $MoO_3(s) + 2OH^-(sol) = [MoO_4]^{2-}(sol) + H_2O(sol)$		-83.83 ± 0.10 (*6*)	-81.70 ± 0.13
(3) $WO_3(s) + 2OH^-(sol) = [WO_4]^{2-}(sol) + H_2O(sol)$		-61.9 ± 0.5 (*5*)	-59.00 ± 0.24 (*5*)
(4) $yMoO_3(s) + (1-y)WO_3(s) = Mo_yW_{1-y}O_3(s)$			
$\Delta H_4 = y\Delta H_2 + (1-y)\Delta H_3 - \Delta H_1$			

TABLE II

ENTHALPIES OF REACTION AND FORMATION OF THE
MIXED MOLYBDENUM TUNGSTEN OXIDES
$Mo_yW_{1-y}O_3$ (298.15 K)

| Compound	ΔH_f° (kJ mole^{-1})	ΔH_4° (kJ mole^{-1})
$Mo_{0.69}W_{0.31}O_3(s)$	-773.35 ± 0.70	$+2.07 \pm 0.36$
$Mo_{0.64}W_{0.36}O_3(s)^a$	-779.75 ± 1.02	$+0.56 \pm 0.83$
$Mo_{0.5}W_{0.5}O_3(s)^a$	-793.82 ± 0.64	$+0.18 \pm 0.30$
$Mo_{0.25}W_{0.75}O_3(s)^a$	-816.62 ± 0.75	$+1.83 \pm 0.23$

^{a} Extrapolated from solution data at 323.15 K.

the former temperature. Reaction was rapid (less than 3 min) and the enthalpies of reaction were calculated using the Dickinson method (9). The enthalpy of reaction of MoO_3 in the reaction medium at 323.15 K was also determined.

The enthalpy change of the reaction

$$yMoO_3(s) + (1 - y)WO_3(s)$$
$$= Mo_yW_{1-y}O_3(s) \quad (4)$$
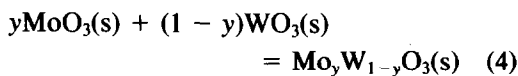
can be calculated using the reaction scheme and the enthalpies of reaction given in Table I. Combining the measured enthalpies of reaction with ΔH_f° (WO_3, 298.15 K) = $-(842.9 \pm 0.8)$ kJ mole^{-1} (10) and ΔH_f° (MoO_3, 298.15 K) = $-(745.1 \pm 0.8)$ kJ mole^{-1} (11, 12), the standard molar enthalpy of formation of $Mo_{0.69}W_{0.31}O_3$ can be calculated. If it is assumed that the enthalpy change of the reaction (Eq. (4)) is the same at 298.15 K as at 323.15 K ($\Delta C_p \sim 0$ using Neumann and Kopp's rule), the standard molar enthalpies of formation of the other mixed oxides may be estimated. The enthalpy change for reaction (Eq. (4)) and the standard molar enthalpies of formation of the mixed molybdenum tungsten oxides are shown in Table II.
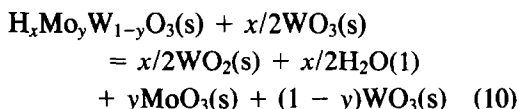
The Hydrogen Insertion Compounds $H_xMo_yW_{1-y}O_3$
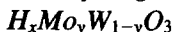
The enthalpies of reaction of six hydrogen insertion compounds were measured.

All but one of the compounds took longer than 3 min to dissolve, and the Regnault–Pfaundler method (9) was used to calculate their enthalpies of reaction. The Dickinson method was used for the rapidly dissolving $H_{0.54}Mo_{0.25}W_{0.75}O_3$. Three of the samples contained a small quantity of the Pt ($\sim 1.6\%$) used in the catalysed reaction of hydrogen with the metal oxide. A correction was made for this, assuming the platinum was as an inert diluent. This assumption has been proved correct by the good agreement of the enthalpy of reaction of $H_{1.66}MoO_3$ containing 5% Pt with the literature value (13).

The overall reaction

$$H_xMo_yW_{1-y}O_3(s) + x/2WO_3(s)$$
$$= x/2WO_2(s) + x/2H_2O(1)$$
$$+ yMoO_3(s) + (1 - y)WO_3(s) \quad (10)$$

was used to determine the enthalpies of formation of the hydrogen insertion compounds $H_xMo_yW_{1-y}O_3$. The complete reaction scheme is shown in Table III. The combination of the enthalpies of solution given in Table III with ΔH_f° (WO_3, 298.15 K) = $-(842.9 \pm 0.8)$ kJ mole^{-1} (10), ΔH_f° (MoO_3, 298.15 K) = $-(745.1 \pm 0.8)$ kJ mole^{-1} (11, 12), ΔH_f° (WO_2, 298.15 K) = $-(589.7 \pm 0.9)$ kJ mole^{-1} (10), and ΔH_f° (H_2O, 298.15 K) = $-(285.83 \pm 0.8)$ kJ mole^{-1} (14) leads to the standard enthalpies of formation for the compounds $H_xMo_yW_{1-y}O_3$ shown in Table IV.

Discussion

The Mixed Oxides $Mo_yW_{1-y}O_3$

The enthalpies of mixing of MoO_3 and WO_3 are small and positive as measured by ΔH_4° for reaction (Eq. (4)). This is not unexpected, since Mo(VI) and W(VI) have similar ionic sizes (the respective 6-coordinate ionic radii are 0.59 and 0.60 Å (15)) and the local octahedral coordination of the metal atoms is retained in the mixed oxides.

TABLE III

CALORIMETRIC REACTION SCHEME FOR $H_xMo_yW_{1-y}O_3$

Reaction	x	y	$\Delta H_{298.15\ K}$ (kJ mole^{-1})	
(5) $H_xMo_yW_{1-y}O_3(s) + (2 + x)OH^-(sol) + x[Fe(CN)_6]^{3-}(sol) = y[MoO_4]^{2-}(sol)$	0.34	0.69	-110.4 ± 1.1	
$+ (1 - y)[WO_4]^{2-}(sol) + x[Fe(CN)_6]^{4-} + (1 + x)H_2O(sol)$	0.45	0.69	-122.5 ± 1.3	
	0.98	0.69	-187.2 ± 1.2	
	0.63	0.50	-144.3 ± 1.3	
	0.66	0.50	-149.2 ± 1.3	
	0.54	0.25	-137.0 ± 1.8	
(6) $MoO_3(s) + 2OH^-(sol) = [MoO_4]^{2-}(sol) + H_2O(sol)$			-83.83 ± 0.10	(6)
(7) $WO_3(s) + 2OH^-(sol) = [WO_4]^{2-}(sol) + H_2O(sol)$			-61.9 ± 0.5	(5)
(8) $WO_2(s) + 4OH^-(sol) + 2[Fe(CN)_6]^{-3}(sol) = [WO_4]^{2-}(sol) + 2[Fe(CN)_6]^{4-}(sol)$				
$+ 2H_2O(sol)$			-356.8 ± 2.1	(16)
(9) $H_2O(l) = H_2O(sol)$			-0.0706 ± 0.0016	(6)
(10) $H_xMo_yW_{1-y}O_3(s) + x/2\ WO_3(s) + x/2\ WO_2(s) + x/2\ H_2O(l) + yMoO_3(s)$				
$+ (1 - y)WO_3(s)$				
$\Delta H_{10} = \Delta H_5 - y\Delta H_6 - (1 - y - x/2)\Delta H_7 - x/2\Delta H_8 - x/2\Delta H_9$				

Thus, the lattice energies of the mixed oxides must differ little from the weighted mean of the lattice energies of the simple oxides. There is no evidence in Salje's phase diagram (1) for the formation of a single preferred intermediate compound and large regions of solid solution exist, as might be expected from the low enthalpy of mixing. The lowest enthalpies of mixing are found in the formation of the zeta phase which is stable at or near to 298 K.

The Hydrogen Insertion Compounds $H_xMo_yW_{1-y}O_3$

In this work the enthalpies of formation of WO_3 and WO_2 have been used as key values. Enthalpies of formation for H_xMoO_3 and H_xWO_3 were originally determined using different reaction schemes (employing $MoO_3(s)/MoO_2(s)$ and $K_3Fe(CN)_6(s)/K_4Fe(CN)_6 \cdot 3H_2O(s)$, respectively). The enthalpies of formation of H_xWO_3 and H_xMoO_3 can be placed on the same base as $H_xMo_yW_{1-y}O_3$ using the reaction scheme in Table III. The values for H_xWO_3 are little changed but the values for H_xMoO_3 are more significantly altered. This is possibly due to some error in ΔH_f° (MoO_2, s, 298.15 K) $= -(588.9 \pm 0.6)$ kJ mole^{-1} (average literature value (11, 12), which disagrees with ΔH_f° (MoO_2, s, 298.15 K) $= -(577.0 \pm 2.7)$ kJ mole^{-1} calculated from the reaction

TABLE IV

ENTHALPIES OF FORMATION, HYDROGEN INSERTION (EQ. (11)), AND OXIDATION (EQ. (12)) AT 298.15 K FOR THE HYDROGEN INSERTION COMPOUNDS $H_xMo_yW_{1-y}O_3$

Compound	ΔH_f° (kJ mole^{-1})	ΔH_{11}° (kJ mole^{-1})	ΔH_{12}° (kJ mole^{-1})
$H_{0.34}Mo_{0.69}W_{0.31}O_3(s)$	-797.74 ± 1.34	-71.7 ± 3.6	-71.2 ± 4.6
$H_{0.45}Mo_{0.69}W_{0.31}O_3(s)$	-803.66 ± 1.54	-67.4 ± 3.2	-75.6 ± 3.8
$H_{0.98}Mo_{0.69}W_{0.31}O_3(s)$	-825.77 ± 1.80	-53.5 ± 1.8	-89.4 ± 2.0
$H_{0.63}Mo_{0.5}W_{0.5}O_3(s)$	-825.76 ± 1.63	-50.7 ± 2.5	-92.2 ± 2.8
$H_{0.66}Mo_{0.5}W_{0.5}O_3(s)$	-825.77 ± 1.64	-48.4 ± 2.4	-94.5 ± 2.7
$H_{0.54}Mo_{0.25}W_{0.75}O_3(s)$	-837.28 ± 2.05	-38.4 ± 3.6	-104.7 ± 4.1

Compound	ΔH_f° (kJ mole^{-1})	ΔH_{11}° (kJ mole^{-1})	ΔH_{12}° (kJ mole^{-1})
$H_{0.28}MoO_3$	-761.61 ± 0.95	-59.0 ± 1.9	-84.0 ± 4.4
$H_{0.34}MoO_3$	-765.6 ± 1.0	-60.3 ± 1.9	-82.6 ± 3.8
$H_{0.93}MoO_3$	-796.1 ± 1.4	-54.8 ± 1.3	-88.1 ± 1.7
$H_{1.68}MoO_3$	-819.0 ± 2.4	-44.0 ± 1.3	-98.9 ± 1.5
$H_{2.0}MoO_3$	-813.5 ± 2.9	-34.2 ± 1.4	-108.7 ± 1.5
$H_{0.18}WO_3$	-847.58 ± 0.99	-26.0 ± 3.2	-116.9 ± 7.1
$H_{0.35}WO_3$	-852.0 ± 1.1	-26.1 ± 2.1	-116.9 ± 3.9

$$MoO_2(s) + WO_3(s) = MoO_3(s) + WO_2(s)$$
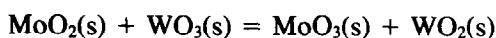
using enthalpies of formation and of reactions given earlier (5, 6, 16) together with ΔH for reaction of MoO_2 with the calorimetric reagent of -293.62 ± 0.58 kJ mole^{-1} (6). The WO_3/WO_2 cycle is preferred because of its good agreement with the hexacyanoferrate(III)/hexacyanoferrate(II) cycle. Recalculated enthalpies of formation are given in Table V.

Enthalpies of hydrogen insertion. Enthalpy changes for the reaction

$$\tfrac{1}{2}H_2(g) + 1/x\, MO_n = 1/x\, H_xMO_n(s) \quad (11)$$
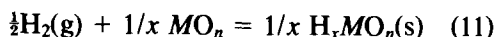
are given in Table IV for the mixed oxides and in Table V for the simple oxides. The exothermicity of hydrogen insertion into the mixed molybdenum tungsten oxides decreases as the tungsten content increases. This is in agreement with the general observation that W(VI) is less oxidising than Mo(VI). For $Mo_{0.69}W_{0.31}O_3$ hydrogen insertion becomes less exothermic as the hydrogen content increases; a similar trend is seen for MoO_3. It is interesting to note that the insertion of hydrogen into $Mo_{0.69}W_{0.31}O_3$ is initially more exothermic than into MoO_3.

Enthalpies of oxidation. Enthalpy changes for the reaction

$$1/x\, H_xMO_n + \tfrac{1}{4}O_2(g)$$
$$= 1/x\, MO_3(s) + \tfrac{1}{2}H_2O(1) \quad (12)$$
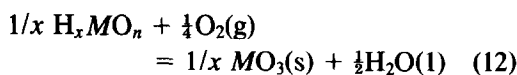
are given in Table IV for the mixed oxides and in Table V for the simple oxides. The large exothermic values for all compounds show that they are all unstable to aerial oxidation. The relative rates of aerial oxidation varied with the exothermicity of this reaction. Although the high tungsten and hydrogen content compounds oxidised rapidly, reduced $H_xMo_{0.69}W_{0.31}O_3$ still had $x > 0.35$ after 3 weeks.

Acknowledgments

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