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Thermochemistry of Hydrogen Molybdenum Bronze Phases H_xMoO_3*

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The enthalpies of formation of five hydrogen molybdenum bronze phases, H_xMoO_3 $(0<x<2)$, have been determined by solution calorimetry. Values obtained for formation from H_2(g) and MoO_3(s) at 298.15°K were (kJ mole^{-1}): $H_{0.28}MoO_3$, -18.2 ± 0.5; $H_{0.34}MoO_3$, -22.5 ± 0.6; $H_{0.93}MoO_3$, -56.5 ± 0.8; $H_{1.68}MoO_3$, -83.9 ± 1.6; and $H_{2.0}MoO_3$, -80.4 ± 2.1. The thermodynamic stabilities of these phases are discussed in relation to their observed electrochemical behavior.

Introduction

MoO_3 has an unusual layer structure in which infinite chains of vertex-sharing MoO_6 octahedra are fused together by edge sharing to form corrugated layers (*1*); the layers are stacked parallel to one another and are separated by a van der Waals gap of ~7 Å. At ambient temperature chemical (*2*) or electrochemical (*3*) reduction in aqueous acidic media leads to the formation of hydrogen molybdenum bronzes H_xMoO_3 $(0<x\leq 2)$. In these compounds hydrogen is inserted into the MoO_3 matrix with only small consequential changes in the lattice parameters of the latter (*4*). Similar insertion compounds, containing lithium and other alkali metals, can be prepared under nonaqueous conditions both by cathodic reduction (*5*) and by chemical methods, using, for example, *n*-butyl lithium as lithiating agent (*6*). Consequently, in both aqueous and nonaqueous media MoO_3 can function as a cathode material which undergoes the reversible redox reaction

$$1/x MoO_3 + A^+ + e = 1/x\, A_xMoO_3$$

$$(A = H, Li).$$

The reduction products H_xMoO_3 are deeply colored, mixed ionic/electronic conductors, which are of interest as cathode materials in electrochromic systems (*7*). The analogous lithium compounds perform the same role in high-power, nonaqueous batteries (*8*).

The hydrogen bronze phases H_xMoO_3 were first systematically investigated by Glemser and co-workers (*2*) and a more complete structural characterization has been published recently by the present authors (*4*).

Four distinct phases are found in the range $0<x\leq 2$. Ranges of homogeneity exist for three of these phases with the approximate limits: blue, orthorhombic, $0.23<x<0.4$; blue, monoclinic, $0.85<x<1.04$; and red, monoclinic, $1.55<x<1.72$. The green, monoclinic, fourth phase of highest hydrogen content approximates the fixed composition $H_{2.0}MoO_3$. The complete structure determination of the first of these phases has been achieved (*9*) and shows H to be attached as –OH bonds to bridging O atoms within an MoO_3 layer. This mode of H atom attachment is similar to that found in the corresponding H_xWO_3 phases (*10*).

The objects of the present work were to determine the enthalpies of formation of the

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phases H_xMoO_3 by means of solution calorimetry and to relate these data to observed electrochemical behavior. A similar thermodynamic study of the related H_xWO_3 system has been published (*11*).

Experimental Materials

Polycrystalline samples of five hydrogen molybdenum bronzes H_xMoO_3 ($x = 0.28$, 0.34, 0.93, 1.68, 1.93) were prepared and characterized by the methods previously described (*4*). The compounds with hydrogen contents 0.28 and 0.34 belonged to the same blue, orthorhombic, phase. The compounds $H_{0.93}MoO_3$ and $H_{1.68}MoO_3$ were, respectively, pure blue and pure red monoclinic phases. The material of analytical composition $H_{1.93}MoO_3$ was shown by X-ray diffraction to be a mixture of green and red monoclinic phases. For calorimetric purposes this material was treated as a mixture of $H_{2.0}MoO_3$ and $H_{1.68}MoO_3$ containing 21.84% by weight of the latter.

MoO_2 was prepared by two methods. The first sample was prepared by reduction of MoO_3 at 550°C for 4 days in a static atmosphere of 0.26 atm H_2 and 3×10^{-2} atm H_2O. The second sample was prepared by heating, at 630°C for 18 hr, a finely ground and vacuum-dried mixture of MoO_3 and Mo powder (Koch Light>99.9%) in a sealed tube. Samples were analyzed by the reducing power method of Choain and Marion (*12*) and by thermogravimetric reductions to Mo metal. Analytical compositions were: Sample I, $MoO_{2.003\pm0.005}$, $MoO_{2.006}$; Sample II, $MoO_{2.020\pm0.009}$, $MoO_{2.010}$. MoO_3 was prepared by heating A/R grade material (>99%) in oxygen at 400°C for 12 hr. Analysis by gravimetric reduction gave $MoO_{3.0\pm0.02}$. Powder X-ray diffraction patterns, of both MoO_3 and MoO_2, revealed no traces of impurities. The calorimetric reaction medium consisted of 40 g $K_3Fe(CN)_6$, dissolved in 1.99 dm^3 of 3.04 *M* KOH solution. It was of nearly identical composition to that used previously (*11*). Samples of air-sensitive H_xMoO_3 compounds were loaded into the calorimeter ampoules under dry nitrogen.

Determination of Enthalpies of Formation

The overall reaction used to determine the enthalpies of formation of H_xMoO_3 was

$$H_xMoO_3(s) = x/2MoO_2(s) + (1 - x/2)MoO_3(s) + x/2H_2O(l). \quad (5)$$

The complete reaction scheme (1–5) is summarized in Table I. Enthalpies of reaction of each component were measured with an LKB 8700 solution calorimeter operated at 298.15°K (25°C) as described previously (*11*). Thirty- to 100-mg charges of solute were dissolved in 100-cm^3 batches of calorimetric reagent. Initially, components from one side of the overall reaction equation were dissolved consecutively with strict stoichiometry into the same solvent. It was subsequently found that the maintenance of strict stoichiometry in the weights of solute added was unnecessary since quite large variations in the sample masses used and in the order of their addition produced no discernible changes in the measured molar enthalpy values. Reaction times for the complete solutions of MoO_3, $H_{0.28}MoO_3$, $H_{0.34}MoO_3$, and $H_{0.93}MoO_3$ were short (<5 min) and Dickinson's method (*13*) was used for the calculation of enthalpies of reaction. In the cases of $H_{1.68}MoO_3$, $H_{1.93}MoO_3$, and MoO_2 reaction periods were longer (5–15 min) and the Regnauld–Pfaundler method was used (*13*). At least five enthalpy of reaction measurements were made on each component. For MoO_2, the two samples prepared by different methods gave values for the enthalpies of reaction which differed insignificantly and a mean value is shown in Table I. Detailed calorimetric data for all runs performed (64) on the various components have been tabulated (*14*). A summary of the values obtained is given in Table I.

TABLE I

CALORIMETRIC REACTION SCHEME FOR H_xMoO_3

Reaction	x	$\Delta H_{298°K}$/kJ mole^{-1}
(1) $H_xMoO_3(s) + x\ Fe(CN)_6^{3-}(sol) + (2+x)\ OH^-(sol)$ $= MoO_4^{2-}(sol) + (1+x)\ H_2O(sol) + x\ Fe(CN)_6^{4-}(sol)$	0.28	−113.18 ± 0.39[a]
	0.34	−119.03 ± 0.50
	0.93	−185.19 ± 0.39
	1.68	−285.1 ± 1.0
	2.0	−343.0 ± 1.6
(2) $MoO_2(s) + 2Fe(CN)_6^{3-}(sol) + 4OH^-(sol)$ $= MoO_4^{2-}(sol) + 2H_2O(sol) + 2Fe(CN)_6^{4-}(sol)$		−293.62 ± 0.58
(3) $MoO_3(s) + 2OH^-(sol) = MoO_3^{2-}(sol) + H_2O(sol)$		−83.83 ± 0.10
(4) $H_2O(l) = H_2O(sol)$		−0.0706 ± 0.0016
(5) $H_xMoO_3(s) = x/2\ MoO_2(s) + (1-x/2)\ MoO_3(s) + x/2\ H_2O(l)$		
$\Delta H_5 = \Delta H_1 - x/2\Delta H_2 - (1-x/2)\Delta H_3 - x/2\Delta H_4$	0.28	+0.03 ± 0.41[b]
	0.34	+0.48 ± 0.52
	0.93	−3.77 ± 0.48
	1.68	−25.0 ± 1.1
	2.0	−49.3 ± 1.7

[a] Uncertainties expressed as twice the standard error of the mean.

[b] Uncertainty is the square root of the sum of the squares of the uncertainties in the individual terms.

Results

Directly determined enthalpy changes for the disproportionation reactions (*5*) are given in Table I. Combination of these data with the standard enthalpies of formation (298.15°K, kJ mole^{-1}) (*15*),

$$\Delta H°_f MoO_3(s) = -745.05 \pm 0.77,$$

$$\Delta H°_f MoO_2(s) = -588.94 \pm 1.05,$$

$\Delta H°_f H_2O(l) = -285.85 \pm 0.04$, leads to values for the standard enthalpies of formation of the compounds studied. These are given in Table II together with standard enthalpy changes (298.15°K) for the following reactions:

$$\tfrac{1}{2}H_2(g) + 1/x MoO_3(s) = 1/x H_xMoO_3(s), \quad (6)$$

$$\tfrac{1}{2}H_2(g) + 1/(x-y)H_yMoO_3(s) = 1/(x-y)H_xMoO_3(s). \quad (7)$$

(x and y represent the compositions of successive phases.)

Discussion

Formation

The enthalpies of formation of H_xMoO_3 from $H_2(g)$ and $MoO_3(s)$ given in Table II are the integral molar enthalpies of solution of hydrogen into MoO_3 and are a measure of the binding energies of hydrogen in the

TABLE II

ENTHALPIES OF FORMATION AND HYDROGENATION AT 298.15°K

Phase	$\Delta H°_f$/kJ mole^{-1}	ΔH_6/kJ mole^{-1}	ΔH_7/kJ mole^{-1}
$H_{0.28}MoO_3$	−763.28 ± 0.79	−65.0 ± 1.8	−65.0 ± 1.8
$H_{0.34}MoO_3$	−767.62 ± 0.84	−66.18 ± 1.8	−66.2 ± 1.8
$H_{0.93}MoO_3$	−801.63 ± 0.80	−60.75 ± 0.86	−57.6 ± 1.4
$H_{1.68}MoO_3$	−829.0 ± 1.4	−49.94 ± 0.95	−36.5 ± 1.7
$H_{2.0}MoO_3$	−825.5 ± 2.0	−40.20 ± 1.0	+10.9 ± 6.3

bronze lattice. The process is exothermic at all compositions. For $x = 0.34$, $\Delta H_6 = -66.18 \pm 1.8$ kJ mole^{-1}; the corresponding value (*11*) for the insertion of hydrogen into WO_3 is -27.4 ± 2.3 kJ mole^{-1} ($x = 0.35$). Thus the binding energy of hydrogen in the parent oxide matrix increases in the sequence $WO_3 < MoO_3$, an order which parallels that found previously for alkali metal oxide bronzes A_xMO_n ($A = \text{Na, K}$) (*16*).

The increasing unfavorability of the stepwise insertion of hydrogen into the MoO_3 matrix is illustrated by the variation of ΔH_7 with x (Table II). Reaction (7) becomes endothermic for the formation of $H_{2.0}MoO_3$ from $H_{1.68}MoO_3$. The entropy change of this reaction approximates that for the loss of gaseous hydrogen (*11*); consequently $\Delta G°$ for the reaction $H_{2.0}MoO_3(s) = H_{1.68}MoO_3(s) + 0.16\,H_2\,(g)$ is negative ($\Delta G° \sim -9.5 \pm 2.0$ kJ mole^{-1}) and the thermodynamic instability of $H_{2.0}MoO_3$ toward dissociation follows. This is consistent with observations. $H_{2.0}MoO_3$ slowly evolves hydrogen at room temperature. At 110°C complete decomposition to $H_{1.68}MoO_3$ takes place. In a similar manner approximate free energy changes can be obtained from the enthalpy data in Table II by neglect of the small entropy differences between solid phases. These in turn may be converted into standard electrode potentials for the process

$$H^+(aq) + e + \frac{1}{(x-y)} H_yMoO_3(s) = \frac{1}{(x-y)} H_xMoO_3(s). \quad (8)$$

The results are shown in Table III.

The rest potential for the couple H^+, MoO_3/H_xMoO_3 (blue orthorhombic) was measured in the cell, Pt, H_2 (1 atm) $|H_2SO_4\,(0.5\,M)|MoO_3$, Pt. The value obtained, 0.471 V, is in good agreement with that calculated for the lowest hydrogen content phase ($x = 0.28$) in Table III,

TABLE III

STANDARD FREE ENERGY CHANGES AND ELECTRODE POTENTIALS (298°K)

x	y	$\Delta G°_7$/kJ mole^{-1}	$E°_8$/V
0.28	0	−45.5	+0.472
0.34	0	−46.7	+0.484
0.93	0.34	−38.1	+0.395
1.68	0.93	−17.0	+0.176
2.00	1.68	+30.4	−0.315

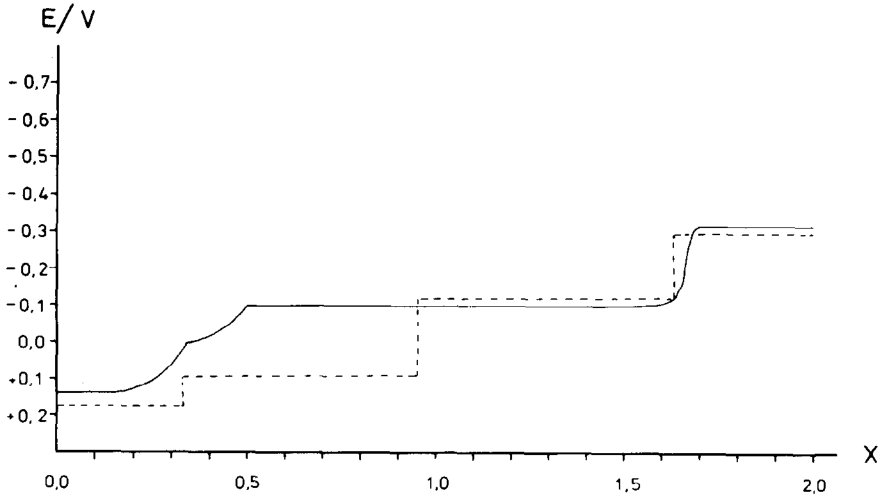

FIG. 1. Variation of electrode potential (E) with electrode composition (x) for MoO_3 electrode in 0.05 M H_2SO_4 electrolyte (versus SCE). (——) Schöllhorn *et al.* (*3*); (– – –) equilibrium data, Table III.

0.472 V. Although no corresponding equilibrium data are available for the higher hydrogen content materials, Schöllhorn *et al.* (*3*) have monitored the potential of a pressed-pellet MoO_3 cathode during discharge under galvanostatic conditions using 0.05 *M* H_2SO_4 as electrolyte (cathodic current ~200 μA). Their voltage versus composition plot is shown in Fig. 1 and superimposed on it is the calculated equilibrium behavior derived from the thermodynamic data of Table III. A succession of two-phase regions occurring with increasing x is assumed. The agreement between calculated and experimental potentials is good at high and low x values. In the intermediate region $0.3 < x < 1.0$ kinetic and equilibrium values diverge and the monoclinic $H_{1.68}MoO_3$ phase is apparently formed earlier than anticipated. This may imply nonuniform reduction within the pellet under dynamic conditions. In the range $1.7 < x < 2.0$ hydrogen evolution occurs as is correctly predicted by the thermodynamic data.

Disproportionation

The data in Table II imply that the phases H_xMoO_3 ($x < 1.7$) are thermodynamically stable with respect to disproportionation to neighboring phases. Indeed the reverse of this reaction provides a useful preparative route to H_xMoO_3. For example, MoO_3 and $H_{1.68}MoO_3$ react together quantitatively (*4*) to form $H_{0.34}MoO_3$ in the proportions $0.798\ MoO_3 + 0.202\ H_{1.68}MoO_3 = H_{0.34}MoO_3$ [5 days, 80°C, in the presence of $H_2O(1)$]. However, with the possible exception of the blue, orthorhombic, phase, all the compounds H_xMoO_3 undergo exothermic decomposition via reaction (5) to MoO_2 and H_2O (Table I). Since the overall entropy change for this reaction is likely to be small and positive (due to the presence of liquid water among the products) the higher hydrogen molybdenum bronzes are nearly certainly metastable; only kinetic constraints permit their existence at ambient temperatures. Above 100°C dehydration of H_xMoO_3 occurs, though in the case of H_2MoO_3 dehydrogenation is favored. In the present work attempted sealed-tube preparations of $H_{0.5}MoO_3$ from Mo, MoO_3, and water at 110°C following Glemser (*2*) lead to mixed products of MoO_3, H_xMoO_3 ($x \sim 0.3$), and MoO_2.

Oxidation

Table IV contains derived thermodynamic data for the oxidation of H_xMoO_3 phases at 298.15°K via

$$1/xH_xMoO_3(s) + \tfrac{1}{4}O_2(g) = 1/xMoO_3(s) + \tfrac{1}{2}H_2O(1). \qquad (9)$$

Again differences among the entropies of solid phases have been ignored.

All phases of H_xMoO_3 are thermodynamically unstable with respect to oxidation at 298°K. At ambient temperatures air oxidation is observed to be rapid for the higher phases of $H_{2.0}MoO_3$ and $H_{1.68}MoO_3$, but in ithe case of the low hydrogen content blue orthorhombic phase the process is very slow. The reluctance of this phase to oxidize electrochemically has also been noted by Schöllhorn *et al.* (*3*) and this must limit its usefulness in an electrochromic system.

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TABLE IV

OXIDATION OF H_xMoO_3 (298°K)

Phase	$\Delta H°_9$/kJ mole^{-1}	$\Delta G°_9$/kJ mole^{-1}
$H_{0.28}MoO_3$	-77.9 ± 1.8	-73
$H_{0.34}MoO_3$	-76.8 ± 1.8	-72
$H_{0.93}MoO_3$	-82.1 ± 0.9	-77
$H_{1.68}MoO_3$	-93.0 ± 0.8	-88
$H_{2.0}MoO_3$	-102.7 ± 1.0	-98

References

1. L. KIHLBORG, *Ark. Kemi* **21**, 357 (1963).
2. O. GLEMSER AND G. LUTZ, *Z. Anorg. Allg. Chem.* **264**, 17 (1951).
3. R. SCHÖLLHORN, R. KUHLMANN, AND J. O. BESENHARD, *Mater. Res. Bull.* **11**, 83 (1976).
4. J. J. BIRTILL AND P. G. DICKENS, *Mater. Res. Bull.* **13**, 311 (1978).
5. J. O. BESENHARD AND R. SCHÖLLHORN, *J. Power Sources* **1**, 267 (1976).
6. M. S. WHITTINGHAM, *J. Electrochem. Soc.* **123**, 315 (1976).
7. R. J. COLTON, A. M. GUZMAN, AND J. W. RABALAIS, *Accounts Chem. Res.* **11**, 170 (1978).
8. F. W. DAMPIER, *J. Electrochem. Soc.* **121**, 656 (1974).
9. J. J. BIRTILL, P. G. DICKENS, AND C. J. WRIGHT, *J. Solid State Chem.*, in press. F. SCHRÖDER AND H. WEITZEL, *Z. Anorg. Chem.* **435**, 247 (1977).
10. P. J. WISEMAN AND P. G. DICKENS, *J. Solid State Chem.* **6**, 374 (1973).
11. P. G. DICKENS, J. H. MOORE, AND D. J. NEILD, *J. Solid State Chem.* **7**, 241 (1973).
12. C. CHOAIN AND F. MARION, *Bull. Soc. Chim. Fr.*, 212 (1963).
13. R. COOPS, R. S. JESSUP, AND K. VAN NES, *in* "Experimental Thermochemistry" (F. D. Rossini, Ed.), Interscience, New York (1956).
14. J. J. BIRTILL, D.Phil. thesis, Oxford University (1978).
15. I. DELLIEN, F. M. HALL, AND L. G. HEPLER, *Chem. Rev.* **76**, 283 (1976); N.B.S. Circular 500 (1952).
16. P. G. DICKENS AND P. J. WISEMAN, *in* "MTP International Review of Science" (L. E. J. Roberts, Ed.), Series Two, Inorganic Chemistry, Vol. 10, p. 211, Butterworths, London (1975).