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VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES. PART XXIV MASS SPECTROMETRIC DETER-MINATION OF THE STABILITY OF GASEOUS MOLYBDATES, TUNGSTATES, MOLYBDITES AND TUNGSTITES OF MAGNESIUM CALCIUM, STRONTIUM AND TIN.

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AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 7350, Task No. 735001

(Prepared under Contract No. AF 61(052)-225 by the Universite Libre de Bruxelles, Brussels, Belgium; G. Verhaegen, R. Colin and J. Drowart)

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FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Non-graphitic." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer.

ABSTRACT

A number of ternary oxides have been identified in the gas phase by mass spectrometry, while vaporizing MgO, CaO, SrO and $SnO_2 + Sn$ from Mo and W crucibles. The approximate stabilities of the gaseous molecules $MgMoO_4$, $CaMoO_4$, $SrMoO_4$, $MgWO_4$, $CaWO_4$, $SrWO_4$, $SrMoO_3$, $CaWO_3$, $CaMoO_3$, $SnWO_4$ and Sn_2WO_5 were deduced from the measurements. The dissociation energies (kcal/mole) into gaseous oxides are:

	$-MoO_3$	$-WO_3$	$-MoO_2$	$-WO_2$
MgO-	147	155	125*	135*
CaO-	168	175	145*	156
SrO-	177	186	156	168
SnO-	125*	132	-	-
2 SnO-	185*	197	-	-

* Estimated

This technical documentary report has been reviewed and is approved.

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INTRODUCTION

Recent mass-spectrometric studies of the vaporization of MgO, CaO and SrO[1], and of a mixture of Sn and SnO_2[2] from Mo and W cells have shown the presence in the gas phase of a number of ternary oxides. Other investigations carried out under similar conditions had shown the presence of gaseous molybdates and tungstates of barium[3], of beryllium[4], of indium[5] and of lithium[6]. Measurements of the stability of such species however have not been made thus far. The present paper reports on the stability of the molecules: $MgMoO_4$, $CaMoO_4$, $SrMoO_4$, $MgWO_4$, $CaWO_4$, $SrWO_4$, $SrMoO_3$, $CaWO_3$, $SrWO_3$, $SnWO_4$ and SnW_2O_5. Other complex gaseous binary oxides of Sn with Mo and W have been identified but their stability was not calculated.

EXPERIMENTAL

The experimental conditions under which the molybdates and tungstates of Mg, Ca and Sr were observed during the vaporization of MgO, CaO and SrO from molybdenum and tungsten cells have been described in a preceding paper[1]. The tin tungstates and molybdates were observed during the vaporization of $Sn+SnO_2$ mixtures from tungsten and molybdenum Knudsen cells in the temperature interval 840 - 950°C. In all instances the gaseous species issuing from the heated cell were collimated, ionized by low-energy electrons (5-25eV) and subsequently mass analyzed in a single focussing 60°, 20 cm radius of curvature instrument equipped with a secondary electron multiplier.

Identification of the molecules.

All the species were identified from their mass, isotopic distribution and appearance potential. A movable beam defining slit intersecting the molecular beam showed all to originate from the Knudsen cell. The ions observed are listed with measured approximate appearance

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potentials (in brackets) in table I. The latter were measured by the linear extrapolation method; the energy scale was calibrated with the known ionization potentials of Mg, Sr and Sn[7] after ascertaining that they did not result from fragmentation of the more complex species by comparing their appearance potential with that of the H_2O^+ ion[8].

The appearance potential and relative intensity data indicated that all the molybdate and tungstate ions, $MMeO_4$ where M denotes Mg, Ca, Sr or Sn, and Me, Mo or W, result from the direct ionization of the corresponding neutral species. The ionization efficiency curves for the ions MO^+, $MMeO_2^+$ and $MMeO_3^+$ indicated that the gaseous molybdates and tungstates also fragment appreciably under electron impact above 13 eV. This was already mentioned previously and taken into account in evaluating partial pressures for the MO molecules[1]. The ionization efficiency curves of the $MMeO_3^+$ ions showed that at low energy they are formed by direct ionization of the corresponding molecules.

The $Sn_2MoO_5^+$, $Sn_2WO_5^+$ and $Sn_3W_2O_9^+$ ions were considered to be parent ions. The other ions between brackets in the $Sn+SnO_2+Mo$ system have not been identified with certainty. The accurate analysis of the isotopic distribution or ionization efficiency curve of the tin molybdates proved difficult because of their low ionic intensity and because their masses superposed with the more abundant binary tin oxide polymer ions and their fragments. It may thus be quite possible that the $Sn_2MoO_8^+$ ion was also present in small concentration. Insufficient resolving power also hindered the isotopic distribution analysis of $Sn_3Mo_2O_3^+$ and $Sn_4Mo_2O_{10}^+$. Because of these experimental difficulties the stability of the tin molybdates was not calculated.

RESULTS AND DISCUSSION

Because of rapid variations in the nature of the condensed phase it was judged preferable, whenever possible, to calculate thermodynamic data from all gas-phase reactions for which only relative pressures are necessary. Thus the stability of the molybdates and tungstates of Mg, Ca and Sr were obtained from the reactions:

$$MMeO_4(g) + 4O(g) \rightleftarrows 4O_2(g) + M(g) + Me(s) \quad (1)$$

$$MMeO_4(g) + 3M(g) \rightleftarrows 4MO(g) + Me(s) \quad (2)$$

$$MMeO_4(g) + 4MeO_2(g) \rightleftarrows 4MeO_3(g) + M(g) + Me(s) \quad (3)$$

Likewise the stability of the molybdites and tungstites of Ca and Sr were derived from the reactions:

$$MMeO_3(g) + 3O(g) \rightleftarrows 3O_2(g) + M(g) + Me(s) \quad (4)$$

$$MMeO_3(g) + 2M(g) \rightleftarrows 3MO(g) + Me(s) \quad (5)$$

$$MMeO_3(g) + 3MeO_2(g) \rightleftarrows 3MeO_3(g) + M(g) + Me(s) \quad (6)$$

No pressure-independant reaction could be used to calculate the stability of $SnWO_4$ and Sn_2WO_5. The reactions used:

$$SnWO_4(g) + 3Sn(s) \rightleftarrows 2Sn_2O_2(g) + W(s) \quad (7)$$

and

$$Sn_2WO_5(g) \rightleftarrows SnWO_4(g) + SnO(g) \quad (8)$$

required absolute pressure calibrations. These were obtained from the known equilibrium constant of the reaction $Sn_2O_2(g) \rightarrow 2SnO(g)$[2].

Because of the variation on the ionic intensity ratios due to changes in composition of the solid phases and also because of the large stoechiometric coefficients of the above equilibria, rather large deviations from the mean values are present in part of the results. This fact and the limited temperature ranges investigated made it difficult to obtain results from a 2nd law treatment

of the data. A 3rd law procedure was therefore adopted to obtain dissociation energies from the measured ionic intensities. This procedure necessitated the estimation of relative ionization cross-sections and secondary electron multiplier yields, as well as the estimation of the free energy functions of all newly identified molecules.

For such complex species about which except for the chemical formula nothing is known, uncertainties due to estimates of relative ionization cross-sections and secondary electron multiplier yields may be relatively important. It was assumed here, for all molecules considered that the relative ionization cross-sections (σ) and additivity rules proposed by Otvos and Stevenson[10] are sufficient approximations. The multiplier yields (γ) were estimated in the usual manner, from a mass-calibration curve corrected for molecular effects[11].

The free energy functions of gaseous O, O_2, Mg, Ca, Sr and of condensed Sn, Mo and W were taken from Stull and Sinke's[12] compilations, those of gaseous MoO_2, MoO_3, WO_2 and WO_3 from De Maria, Burns, Drowart and Inghram[9] and those of gaseous MgO, CaO and SrO from Brewer and Chandrasekharaiah[13] as discussed previously[1]. The free energy function of gaseous SnO was taken from Kelley and King[14], that of Sn_2O_2 was deduced from the data for the $Sn_2O_2(g) \rightarrow 2SnO(g)$ equilibrium[2]. For consistency the enthalpies of formation of MoO_2, MoO_3, WO_2 and WO_3 and Sn_2O_2 were taken from the same sources as the free energy functions.

The free energy functions of the gaseous molybdates, tungstates, molybdites and tungstites were calculated from usual statistical mechanical formulae[15].

A nearly tetrahedral arrangement of O atoms around the Mo and W atoms has been adopted for the tungstates and molybdates by analogy with the structure in the condensed phases and in the $MoO_4^=$ and $WO_4^=$ ions in solution[16]. The interatomic distance Mo-O and W-O were taken the same as in crystaline Li_2WO_4[17]. The Mg, Ca, Sr and Sn

atoms were supposed attached to two of the O atoms forming planar closed structures. Interatomic distances, Mg-O, Ca-O, Sr-O, Sn-O, Mo-O and W-O were estimated to be the same as in the corresponding molecules[13,18]. Of the 12 vibration frequencies, 9 were taken identical to those of the $MoO_4^=$ and $WO_4^=$ ions[16]. They are 218 (doubly degenerate, d.d.), 360 (triply degenerate, t.d.), 944, 896 (t.d.) cm^{-1}. The remaining 3 were estimated to be 300 cm^{-1}(d.d.) and 700 cm^{-1}.

The model assumed for the gaseous molybdites and tungstites is in many ways analogous to that for the molybdates and tungstates. These molecules were assumed to have planar closed structures with the same interatomic distances, but with only 3 oxygens surrounding the Mo or W atoms. Six of the vibration frequencies were taken by analogy with $MoO_4^=$ and $WO_4^=$. They are 218(t.d.) and 896(t.d.) cm^{-1}. The other 3 were estimated to be 300 cm^{-1}(d.d.) and 700 cm^{-1}.

The electronic partition functions of the gaseous molybdates and tungstates were assumed to be the same as for MoO_3 and WO_3[9] and those of the gaseous molybdites and tungstites equal to those of MoO_2 and WO_2[9].

Free energy functions were calculated in detail for gaseous $MgWO_4$, $SrWO_4$, $SrWO_3$ and $SrMoO_3$, the values for the other molecules were estimated by analogy. The numerical values (in cal/mol°K) for the binary oxides of Mg, Ca and Sr are tabulated in Table 2 for different temperatures. The values estimated for $SnWO_4$ are 88,90 and 92 cal/mole°K at 1100, 1200 and 1300°K respectively, while a value of 120 cal/mole°K at 1200°K was estimated for Sn_2WO_5.

The enthalpies of the reaction 1-8 are given in Table 3. For each molecule the equilibrium considered is given along with the accompanying enthalpy change (col.2), the number of experimental points (col.3) and the dissociation energy into oxides obtained

therefrom (col.4) through use of thermochemical cycles. The auxiliary data used to obtain the dissociation energies are:

$O_2(g) \rightarrow 2O(g)$	$D_o^o = 117.96$ kcal/mole	(12)
$MgO(g) \rightarrow Mg(g)+O(g)$	$D_o^o = 85.0$ kcal/mole	(1)
$CaO(g) \rightarrow Ca(g)+O(g)$	$D_o^o = 92.2$ kcal/mole	(1)
$SrO(g) \rightarrow Sr(g)+O(g)$	$D_o^o = 101.9$ kcal/mole	(1)
$MoO_3(g) \rightarrow 3O(g)+Mo(s)$	$\Delta H_o^o = 254.0$ kcal/mole	(9)
$WO_3(g) \rightarrow 3O(g)+W(s)$	$\Delta H_o^o = 243.3$ kcal/mole	(9)
$MoO_2(g) \rightarrow 2O(g)+Mo(s)$	$\Delta H_o^o = 104.4$ kcal/mole	(9)
$WO_2(g) \rightarrow 2O(g)+W(s)$	$\Delta H_o^o = 96.0$ kcal/mole	(9)
$Mo(s) \rightarrow Mo(g)$	$\Delta H_o^o = 157.1$ kcal/mole	(12)
$W(s) \rightarrow W(g)$	$\Delta H_o^o = 199.7$ kcal/mole	(12)
$Sn(s) \rightarrow Sn(g)$	$\Delta H_o^o = 72.0$ kcal/mole	(12)
$SnO(g) \rightarrow Sn(g) +O(g)$	$D_o^o = 125.8$ kcal/mole	(2)
$Sn_2O_2(g) \rightarrow 2SnO(g)$	$D_o^o = 69.7$ kcal/mole	(2)

The proposed dissociation energies of the gaseous binary oxides into their constituent oxides are given in column 6.

The error limits given in Table 3, col.4 are statistical 95% probabilities: $\sigma = 2\left(\frac{\Sigma\epsilon^2}{n-1}\right)^{1/2}$. For the reasons given above, these are quite large in some cases. The values obtained for the dissociation energies (col.5) however are in most cases in satisfactory agreement. The error limits given in col.5 further include possible systematic errors. A factor of 2.5 has been allowed for the $\sigma\gamma$ products, a factor of 2 in the ionizing electron voltage corrections[1] and 1% in the temperature, the different possible sources of error being considered to be independent of one another. With the average statistical deviations the uncertainty in the change in free energy (ΔG_T^o) accompanying the dissociative reactions:

$MMeO_{3,4}(g) \rightarrow MO(c) + MeO_{2,3}(g)$ is ±7 kcal/mole. Overall uncertainties of ±15 kcal/mole are estimated for the reaction enthalpies by assuming the changes in free functions to be accurate within 6 cal/mole°K. The relative values of the stability molecules are probably correct within ±8 kcal/mole.

The atomization energy of these species can be calculated by coupling the reaction enthalpies given in Table 3 with the data presented above. The values (in electron volts) are:

$\Delta H^{o}_{oat}(MgMoO_4) = 27.9 \pm 1.0$ eV

$\Delta H^{o}_{oat}(CaMoO_4) = 29.1 \pm 1.0$ "

$\Delta H^{o}_{oat}(SrMoO_4) = 30.0 \pm 1.0$ "

$\Delta H^{o}_{oat}(MgWO_4) = 29.6 \pm 1.0$ "

$\Delta H^{o}_{oat}(CaWO_4) = 30.8 \pm 1.0$ "

$\Delta H^{o}_{oat}(SrWO_4) = 31.7 \pm 1.0$ "

$\Delta H^{o}_{oat}(MgMoO_3) = 20.3 \pm 1.5$ "*

$\Delta H^{o}_{oat}(CaMoO_3) = 21.4 \pm 1.5$ "*

$\Delta H^{o}_{oat}(SrMoO_3) = 22.3 \pm 1.0$ "

$\Delta H^{o}_{oat}(MgWO_3) = 22.5 \pm 1.5$ "*

$\Delta H^{o}_{oat}(CaWO_3) = 23.6 \pm 1.0$ "

$\Delta H^{o}_{oat}(SrWO_3) = 24.5 \pm 1.0$ "

$\Delta H^{o}_{oat}(SnMoO_4) = 28.7 \pm 1.5$ "*

$\Delta H^{o}_{at}(SnWO_4) = 30.4 \pm 1.0$ "

$\Delta H^{o}_{oat}(Sn_2MoO_5) = 36.8 \pm 2.0$ "*

$\Delta H^{o}_{oat}(Sn_2WO_5) = 38.7 \pm 1.5$ "

* Estimated.

All the molecules for which dissociation energies into oxides are given show a surprising stability, which is possibly due to important ionic contributions in the intramolecular forces. The behavior of these molecules under electron impact is also comparable to that of other "ionic" molecules such as the alkali halides[19] and the metaborates[20] and could be another argument in the same direction.

The stability of such molecules reflects on the other hand their importance in vaporization processes of oxides in the presence of molybdenum or tungsten and the need to take their presence into account in the interpretation of weight loss experiments.

The identification of such molecules indicates further the interest of extending mass spectrometric studies, which have until now been performed mainly for binary compounds to ternary compounds.

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TABLE 1.

Ions observed and approximate appearance potentials (eV)

System	T°K	Ions
MgO+Mo	2100	Mg^+, MgO^+, O^+(14.0), O_2^+(11.9), MoO^+, MoO_2^+(9.2) MoO_3^+(11.8), $MgMoO_3^+$, $MgMoO_4^+$.
MgO+W	2100	Mg^+, MgO^+, O^+, O_2^+, WO_2^+(9.8), WO_3^+(11.9), $MgWO_3^+$, $MgWO_4^+$.
CaO+Mo	2400	Ca^+, CaO^+(6.5), O^+, O_2^+, MoO^+, MoO_2^+, MoO_3^+, $CaMoO_3^+$, $CaMoO_4^+$.
CaO+W	2300	Ca^+, CaO^+, O^+, O_2^+, WO_2^+, WO_3^+, $CaWO_3^+$(6.7), $CaWO_4^+$(9.8).
SrO+Mo	2150	Sr^+, SrO^+(6.1), Sr_2O^+(4.8), O^+, O_2^+, MoO^+, MoO_2^+, MoO_3^+, $SrMoO_2^+$(11.0), $SrMoO_3^+$(6.2), $SrMoO_4^+$(9.2).
SrO+W	2200	Sr, SrO^+, Sr_2O^+, O^+, O_2^+, WO_2^+, WO_3^+, $SrWO_3^+$(6.4) $SrWO_4^+$(9.4).
Sn+SnO_2+Mo	1200	Sn^+, SnO^+(10.5), Sn_2O^+(14.0), $Sn_2O_2^+$(9.8), $Sn_3O_2^+$, $Sn_3O_3^+$(9.8), $Sn_4O_3^+$, $Sn_4O_4^+$(9.2), $SnMoO_3^+$, $SnMoO_4^+$, $Sn_2MoO_5^+$, $Sn_3MoO_6^+$, ($SnMo_2O_7^+$), ($Sn_3Mo_2O_9^+$), ($Sn_4Mo_2O_{10}^+$).
Sn+SnO_2+W	1200	Sn^+, SnO^+, Sn_2O^+, $Sn_2O_2^+$, $SnWO_3^+$, $SnWO_4^+$(10.8), $Sn_2WO_5^+$(8.4), $SnW_2O_7^+$, $Sn_2W_2O_8^+$, $Sn_3W_2O_9^+$.

TABLE 2.

Estimated values (in cal/mole degree) of the free energy functions of the gaseous molybdates, tungstates, molybdites and tungstites of Mg, Ca and Sr.

T°K / Molecule	2000	2100	2200	2300	2400
$MgMoO_4$	105.3	106.5	107.8	109.0	110.2
$CaMoO_4$	106.6	107.8	109.1	110.3	111.5
$SrMoO_4$	107.8	109.1	110.4	111.6	112.8
$MgWO_4$	103.9	105.2	106.4	107.6	108.8
$CaWO_4$	105.2	106.5	107.7	108.9	110.1
$SrWO_4$	106.4	107.7	109.0	110.2	111.4
$SrMoO_3$	105.3	106.5	107.7	108.8	109.9
$CaWO_3$	105.0	106.2	107.3	108.4	109.4
$SrWO_3$	106.4	107.6	108.7	109.8	110.8

TABLE 3. Dissociation energy of molybdates, tungstates, molybdites ans tungstites of Mg, Ca, Sr and Ba into oxides (kcal/mole)

Molecule	Equilibrium	no exp. points	ΔH^{o}_{o}	$D^{o}_{o}(MO-MeO_{2,3})$	Proposed value
$MgMoO_4$	$MgMoO_4+3Mg \rightarrow 4MgO+(Mo)$[a]	1	141.3	142.3	147±15
	$MgMoO_4+4MoO_2 \rightarrow Mg+4MoO_3+(Mo)$	1	-107.0	152.4	
$CaMoO_4$	$CaMoO_4+4MoO_2 \rightarrow Ca+4MoO_3+(Mo)$	2	- 84.6±6.6	167.6	168±15
$SrMoO_4$	$SrMoO_4+3Sr \rightarrow 4SrO+(Mo)$	7	122.0±4.0	173.7	177±15
	$SrMoO_4+4MoO_2 \rightarrow Sr+4MoO_3+(Mo)$	6	- 62.3±3.1	180.2	
$MgWO_4$	$MgWO_4+3Mg \rightarrow 4MgO+(W)$	3	142.2±5.0	153.9	155±15
	$MgWO_4+4WO_2 \rightarrow Mg+4WO_3+(W)$	5	-105.3±1.6	155.6	
$CaWO_4$	$CaWO_4+4O \rightarrow 4O_2+Ca+(W)$	1	37.2	173.5	175±15
	$CaWO_4+3Ca \rightarrow 4CaO+(W)$	5	141.3±3.0	174.6	
	$CaWO_4+4WO_2 \rightarrow 4WO_3+Ca+(W)$	4	- 76.2±10.1	177.5	
$SrWO_4$	$SrWO_4+4O \rightarrow 4O_2+SR+(W)$	4	55.8±21.0	182.4	186±15
	$SrWO_4+3Sr \rightarrow 4SrO+(W)$	4	131.7±6.1	194.1	
	$SrWO_4+4WO_2 \rightarrow 4WO_3+Sr+(W)$	3	- 61.5±3.7	182.5	

TABLE 3. Continued

Molecule	Equilibrium	no exp. point	ΔH°_{o}	$D^{\circ}_{o}(MO-MeO_{2,3})$	Proposed value
$SrMoO_3$	$SrMoO_3+2Sr \rightarrow 3Sr+(Mo)$	3	56.6±2.0	156.0	156±15
	$SrMoO_3+3MoO_2 \rightarrow 3MoO_3+Sr+(Mo)$	3	-85.7±2.8	156.8	
$CaWO_3$	$CaWO_3+2Ca \rightarrow 3CaO+(W)$	2	66.5±3.0	154.9	156±15
	$CaWO_3+3WO_2 \rightarrow 3WO_3+Ca+(W)$	2	-95.8±1.9	157.9	
$SrWO_3$	$SrWO_3+3O \rightarrow 3O_2+Sr+(W)$	1	112.8	168.8	168±15
	$SrWO_3+2Sr \rightarrow 3SrO+(W)$	1	63.9	171.7	
	$SrWO_3+3WO_2 \rightarrow 3WO_3+Sr+(W)$	1	-81.9	162.1	
$SnWO_4$	$SnWO_4+3Sn \rightarrow 2Sn_2O_2+(W)$	5	74.0±3.0	131.5	132±15
SnW_2O_5	$SnW_2O_5 \rightarrow SnWO_4+SnO$	5	65.6±0.9	-	-

(1) bracketted symbols represent elements at unit activity and in the condensed phase; unbracketted symbols represent gaseous species.

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