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A LITERATURE SURVEY OF THE FLUORIDES AND OXYFLUORIDES OF MOLYBDENUM

C. F. Weaver H. A. Friedman

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OAK RIDGE NATIONAL LABORATORY Oak Ridge, Tennessee operated by UNION CARBIDE CORPORATION for the U.S. ATOMIC ENERGY COMMISSION

A LITERATURE SURVEY OF THE FLUORIDES AND OXYFLUORIDES OF MOLYBDENUM C. F. Weaver and H. A. Friedman

INTRODUCTION

Molybdenum is one of the more important fission products with respect to the amount produced as well as its thermal neutron absorption cross section. Consequently the chemical behavior of molybdenum and its fluorides in molten salt reactor fuels which are in contact with graphite and Hastelloy is of interest.^{1,2,3} A research program to determine the extent and rate of the pertinent reactions has recently been initiated. The necessary literature review of the fluorides and oxyfluorides of molybdenum is summarized in this report for the convenience of others.

MoF₃

Reported methods for the synthesis of MoF₃ are:

- 1. $MoBr_3 + 3HF \rightarrow MoF_3 + 3HBr$ at 600° in a Pt boat enclosed in a Cu tube.⁴
- 2. $2MO + 6HF \frac{225^{\circ}C}{24} hrs 2MOF_3 + 3H_2.^5$
- 3. $MoF_5 + Mo \rightarrow MoF_3$ at 400°C in a Ni capsule.⁶
- 4. $MoF_5 + SbF_3 \rightarrow MoF_3 + ?$. The SbF₃ was carried in a stream of A at 150 to 200°C.⁶

The product produced by method (1) has different properties than that of methods (3) and (4). The authors of reference 6 stated that products similar to that obtained by method (1) were produced under hydrolyzing conditions. The properties of both materials are described below. Although it is possible for MoF_3 to exist in two crystalline forms, it is more likely that the product described in reference 4 is an oxyfluoride. Properties reported for "MoF₃" from method (1) are: non-hygroscopic, dark pink, shows no evidence of melting or subliming at 800° C in the absence of air, is isostructural with ReO₃ and TaF₃ (cubic, space group Pm3m, a = 3.8985 ± 0.005) at $<800^{\circ}$, has a distorted structure at $>800^{\circ}$ ⁷ and is reduced by H₂ to Mo metal.⁴ The material produced by method (2) was found to be cubic by x-ray analysis⁵ and is probably the same as the product of method (1).

Properties reported⁶ for MoF_3 from methods (3) and (4) are: variable color (ochre, light-green, gray, black, dark red, yellowish tan), stable to at least 900° in Ni under its own pressure, stable to 500° under vacuum, disproportionates above 600° to form Mo metal and higher fluorides, density 4.64 ± 0.07 g/cm³ (measured), 4.50 g/cm³ (x-ray) and VF₃ type structure (space group R3c) determined by x-ray and neutron diffraction. Other workers (ref. 8) have confirmed that MoF₃ has a bimolecular rhombohedral unit cell with the R3c space group. They have also shown that the compound is antiferromagnetic below 185° K. The trace of a neutron diffraction powder pattern taken at 4.2° K may be found in this reference.

MoF_4

Reported methods for synthesis of MoF_4 are:

- 1. $2MO(CO)_6 + 3F_6 \frac{75^0}{2} 2MO_2F_9 + 12CO; MO_2F_9 \frac{170^0}{2} MOF_4 + MOF_5$
- 2. Same as above except that the temperatures were -65° and 100° , respectively.¹⁰
- 3. $Mo(CO)_6 + MoF_6 \rightarrow MoF_5 + MoF_4 + CO;$ volatile products removed by vacuum. 10,11

4.
$$MOF_5 > 150^{\circ} MOF_6 + MOF_4$$
.

This compound has been described as light green, 9,11 non-volatile, 9,10,11 and immediately hydrolyzable with H₂0.⁹

3

$Mo_2 F_9$

An olive green solid of this composition has been reported, 9,10 but the authors of reference 9 suggested that it was a mixture rather than a single compound. It was prepared by the reactions: $4Mo(CO)_6 + 9F_2 \xrightarrow{-65} to -75^{\circ} 2Mo_2F_9 +$ $100 - 170^{\circ}$ 24CO and disproportionates by the reaction: Mo_2F_9 $MOF_4 + MOF_5$.

MoF₅

MoF₅ is a yellow hygroscopic substance which melts to form a yellow viscous liquid.^{9,11} It fumes in air forming blue hydrolysis products, but is stable in air dried with The viscosity and high Trouton constant of MoF_5 are P₂O₅. explained by assuming self ionization: $2MoF_5 \rightarrow MoF_4^+ + MoF_6^{-2}$ This compound has been synthesized by:

- $Mo_2F_9 \xrightarrow{100-170^{\circ}} MoF_4 + MoF_5.^{9,10}$ 1.
- $2MoF_6 + PF_3 \xrightarrow{amb} 2MoF_5 + PF_5$. 12-142.
- $\begin{array}{rll} \text{Mo} + \text{F}_2 \rightarrow \text{MoF}_6 & + \text{"residue", "residue", distill} \\ \text{Mo(CO)}_6 & + \text{MoF}_6 & \stackrel{25^\circ}{\longrightarrow} & \text{MoF}_5 & + & \text{MoF}_4 & + & \text{CO.} \\ \end{array} \begin{array}{r} \text{MoF}_5 & \text{MoF}_5 & \text{MoF}_5 & + & \text{MoF}_4 & + & \text{CO.} \end{array}$ 3.
- 4.
- $W(CO)_6 + MoF_6 \rightarrow MoF_5 + WF_4 + CO.$ ¹¹ 5.
- 6. $Mo(CO)_6 + F_2 = -\frac{65}{2} MoF_5 + (?)$
- 11 $MOF_6 + MO \rightarrow MOF_5$. 7.
- $WF_4 + 2MoF_6 \xrightarrow{amb} 2MoF_5 + WF_6$. 8.

MoF₅ disproportionates irreversibly (>150°) below its boiling point to form MoF_4 and MoF_6 .^{10,11} Its vapor pressure in the range 70.0 to 160° is given by log P = 8.58 - 2772/T.¹⁰ Table I provides a summary of the properties of MoF₅. MoF₅ dissolves in MoF₆ to form a yellow solution.¹² It is monoclinic (space group C2m) with $a = 9.61 \pm 0.01 \text{\AA}$, $b = 14.22 \pm$ $0.02\ddot{A}$, c = 5.16 ± 0.01 \ddot{A} , and β = 94° 21' ± 20'.¹¹ An electron density projection on the 001 plane and a table of interatomic distances may also be found in reference 11. MoF₅ will reduce UF₆ to UF₅ in excess UF₆ and to UF₄ in excess MoF₅.¹⁴

MMoF₆

The compounds $MMOF_6^{15}$ (M = Na, K, Rb, Cs) were formed by: $2MOF_6 + 2MI \xrightarrow{-60^0} I_2 + 2MMOF_6$ and the impurities removed by exposure to vacuum at 200° C. All of these compounds form white crystals which are stable at 250° C, but attack glass above 250° C and turn blue in moist air. KMOF₆ has a magnetic moment of 1.24 Bohr magnetons at 25° C, the low value being attributed to spin orbit coupling. The Na, Rb, and Cs compounds are cubic with a = 8.20, 5.11, and 5.29Å, respectively. The K compound is tetragonal with a = 10.17 and c = 9.97Å.¹⁵ The Mo-F distance in NaMoF₆ is 1.74 ± 0.03Å.¹¹ The Na compound has been further studied (ref. 16) and found to be face centered cubic, space group Fm3m (O⁵_h, No. 255). All of the interatomic distances are listed in this report.

K₂MoOF₅

The compound $K_2 MoOF_5$ has been reported¹⁵ to be a readily hydrolyzed pale green solid.

MoF_6

Molybdenum hexafluoride has been synthesized by: 1. $F_2 + Mo \xrightarrow{60-400^{\circ}} MoF_6^{4,10,12,17-21}$ in Pt boat in Ni or Cu. F_2 diluted with N_2 .

- 2. Mo + BrF₃ \rightarrow MoF₆ + ?.²²
- 3. Mo + ClF₃ \rightarrow MoF₆ + ? in Ni boat.²⁰
- 4. $MoCl_5 + HF \rightarrow MoF_6 + ?.^{20}$

The MoF₆ is purified by trap to trap distillation over NaF.^{12,17,23} The reactivity of MoF₆ with respect to fluorination has been described^{13,14} as: $CrF_5 > UF_6 > MoF_6 > WF_6$. It forms a white solid^{18,24} and a colorless liquid.^{19,20,24,25} The colorless gas consists of octahedral molecules²⁴⁻²⁷ with d²sp³ hybrid bonds, has a bond strength of 105Kcal/mole^{13,28} and has a second virial coefficient of -923 cm³/mole.²¹ The Mo-F bond has a reported length of 1.83\AA^{29-31} , 840\AA^{27} 1.830Å, ³² and a stretching force constant of 5.00, ³⁰ 5.13, ¹³ 4.73, ^{14,23} 5.087, ²⁵ 5.080, ³⁴ 4.9972, ³⁵ 4.9875, ³⁶ (x 10⁻⁵ dynes/cm). The physical, structural, and thermal properties of MoF₆ are summarized in Tables II-VII. Traces of the Raman, ^{19,25,27} infrared, ^{19,24,27} ultraviolet, ²⁵ and nuclear magnetic resonance ³⁷ spectra of MoF₆ have been reported.

The values of Cp^0 , S^0 , $H^0 - H_0^0$, $-(F^0 - H_0^0)/T$ for gaseous MoF_6 in the ideal state have been calculated from the fundamental frequencies over the temperature range $50-1600^0$ K and are tabulated in references 21, 24, 27, 31, and 38.

The values of Cp determined calorimetrically for solid and liquid MoF₆ from 50 to 298.5^oK are tabulated in reference 39. The enthalpy and entropy of gaseous MoF₆ from 400 to 2000^oK are tabulated⁴⁰ and summarized as $H_T - H_{298.15} =$ 35.80T + 0.59 x 10⁻³T² + 6.97 x 10⁵T⁻¹ - 13,064 (298-2000^oK, gas)⁴⁰ and Cp = 35.80 + 1.18 x 10⁻³T - 6.97 x 10⁵T⁻².⁴⁰ The functions Cp⁰, S⁰, H⁰ - H⁰₀, -(F⁰ - H⁰₀)/T are also tabulated in reference 21 for solid 5-290.70^oK, liquid 290.76 - 350^oK, and gas 50 - 1000^oK. The values for the solid and liquid are based on calorimetric data. Those for the gas are based on a combination of calorimetric and spectroscopic data.

The System MoF₆-UF₆

The system MoF_6-UF_6 has a eutectic at 22 M/O UF₆ and 13.7°C, and incomplete solid solution.⁴¹ A phase diagram of the system may be found in reference 41.

M₂MoF₈

The family of compounds $M_2 MoF_8$ (M = K, Rb, Cs) has been reported.²² The authors of reference 22 tried but failed to synthesize the sodium analog.

6

$MoOF_4$

The compound $MoOF_4^{4,10,33,42}$ tends to hydrolyze in air,³³ but is stable in glass to at least 180°. Its vapor pressure is given by the following relations:

 $\log P = 8.716 - 2671/T$ for liquid, $95-185°C^{10}$

 $\log P = 9.21 - 2854/T$ for solid $40-95°C^{10}$

Other physical and thermodynamic properties of this material are summarized in Table VIII.

$MOO_2 F_2$

The compound $MoO_2F_2^{33,42}$ sublimes with decomposition at ~270°C⁴² and tends to hydrolyze in air.³³

Container Materials

The fluorides of molybdenum react readily with moisture. Hence the systems in which they are handled must be scrupulously dried by outgasing, flaming, or baking. The following container materials have been used with molybdenum fluorides:

Material	Reference
Cu	12,18-21
Ni	13,18-21,23,41
Pt	18,23
Monel	21,23,41
Brass	41
Glass, pyrex, quartz	12,13,17,18,20,24
Fluoethane	19
Kel-F tubes	13,14
Teflon	13,18,20,21,23,41

Fluorinated greases have been used, 18 but packless all metal values are to be preferred. 12 The use of NaF as an HF getter will allow storage of MoF₆ in glass at room temperature for many days without etching. 18,20 In general, glass and plastic type materials are useful to about 200°C above which the metals are necessary.

TABLE I

Physical Properties of MoF₅

М. Р.	64°, ^{a, b} 67 ^{c}
B. P.	213.6°, ^d 211 ^c
т. Р.	67.0°, pressure very low ^G
ΔH vaporization	12,370 cal/mole ^d
$\Delta S_{vaporization}$	25.4 cal/mole/deg. ^d
Vapor pressure	~2mm (at 65°) ^C
Density	3.44 (measured, solid) ^C
Density	3.61 (x-ray) ^C

^aR. D. Peacock, "Two New Fluorides of Molybdenum," Proc. Chem. Soc., 59 (1957).

^bD. E. LaValle, R. M. Steele, M. K. Wilkinson and H. L. Yakel, Jr., "The Preparation and Crystal Structure of Molybdenum (III) Fluoride," J. <u>Am. Chem. Soc. 82</u>, 2433-4 (1960).

^CA. J. Edwards, R. D. Peacock, and R. W. H. Small, "The Preparation and Structure of Molybdenum Pentafluoride," J. Chem. Soc., 4486-91 (1962).

^dGeorge H. Cady and George B. Hargreaves, "Vapor Pressures of Some Fluorides and Oxyfluorides of Molybdenum, Tungsten, Rhenium, and Osmium," J. <u>Chem. Soc.</u>, 1568-74 (1961).

TABLE II

Thermal and Structural Properties of MoF₆ 17,^a 17.4,^{b-d} 17.5,^e 17.4±0.5°C^f M. P. 35,^{a,c,g} 34.0°C^h B. P. 17.5°C & 406.5mm, ^{C,g} 17.4 & Т. Р. 398.1mm -9.6, e,d -9.8±0.5^f & 104.7mm,^h Solid-Solid Transition bcc a = $6.23 \text{Å}^{0} \text{f}, \text{i}$ High Temperature Form orthorhomic^{f,i} Low Temperature Form at $-20^{\circ}C$ $a = 9.65 \pm .02A$ $b = 8.68 \pm .03A$ $c = 5.05 \pm .02A$ ^aOtto Ruff and Fritz Eisner, "Uber die Darstellung und Eigenschaften von Fluoriden des Sechswertigen Molybdans," Berichte 40, 2926-35 (1907). ^bT. A. O'Donnell, "The Preparation and Manipulation of Molybdenum Hexafluoride," J. Chem. Soc., 4681-2 (1956). ^CN. S. Nikolaev and A. A. Opalovskii, "Solubility Isotherm at 0° of the HF-MoF₆-H₂O System," Russian J. Inorg. Chem. 4, 532-6 (1959). ^dBernard Weinstock, "Some Properties of the Hexafluoride Molecules," Record Chem. Progress 23, 23-50 (1962). ^eA. P. Brady, O. E. Myers, and J. K. Clauss, "Thermodynamic Properties of High Fluorides. 1. The Heat Capacity, Entropy and Heats of Transition of Molybdenum Hexafluoride and Niobium Pentafluoride," J. Phys. Chem. 64, 588-91 (1959). f L. E. Trevorrow, M. J. Steindler, D. V. Steidl, and J. T. Savage, "Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes. Part XIII. Condensed-Phase Equilibria in the System Molybdenum Hexafluoride - Uranium Hexafluoride," ANL-7240, August 1966. ^gVon Otto Ruff and Ernst Ascher, "Einige Physikalsiche Kon-stanten von SiF₄, WF₆, and MoF₆," <u>Zeitschrift fur anorgan-</u> ische und allgemeine Chemie. Band 196, 413-20 (1931). ^hGeorge H. Cady and George B. Hargreaves, "The Vapor Pressures of Some Heavy Transition-metal Hexafluorides," J. Chem. Soc., 1563-68 (1961). ¹Darrell Osborne, Felix Schreiver, John G. Malm, Henry Selig, and Leon Rochester, "Heat Capacity and Other Thermodynamic Properties of MoF₆ Between 4⁰ and 350⁰K," J. Chem. Physics 44, 2802-9 (1966).

TABLE 1	1	Ι
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Dens	Lty	of	MoF ₆
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Density,	High Temp	. Solid	8°C	2.91 g/cc (measured) ^a
11	** **	**	0°C	2.88 " "
"	** **	**	10°C	2.88 " (x-ray)
17	** **	**	278°K	$2.88 \pm 0.04 (x-ray)^{b}$
11	Low "	**	237°K	3.27 ± 0.03 "
11	Liquid		17.5°C ^c	2.551 g/cm ³
11	**		19°C	2.543 "
11	**		27°C	2.503 "
**	**		34°C	2.470 "
11	11		17.4°C d	2.551 "
d(Low Ter	mp. Solid)	for 77.16	5 to 237°K	$= 3.619 - 0.00 \ 130T \ (g/cm^3)^{b}$
d(High Te	emp. Solid)		$= 3.464 - 0.00210T (g/cm^3)^{D}$
d(Liquid)) for 294.	33 to 344.	63°K	$= 3.733 - 0.00404T (g/cm^3)^{b}$

^aL. E. Trevorrow, M. J. Steindler, D. V. Steidl, and J. T. Savage, "Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes. Part XIII. Condensed-Phase Equilibria in the System Molybdenum Hexafluoride and Uranium Hexafluoride," ANL-7240, August 1966.

^bDarrell Osborne, Felix Schreiver, John G. Malm, Henry Selig and Leon Rochester, "Heat Capacity and Other Thermodynamic Properties of MoF₆ Between 4⁰ and 350[°]K," J. Chem. Physics 44, 2802-9 (1966).

^CVon Otto Ruff and Ernst Ascher, "Einige Physikalische Konstanten von SiF₄, WF₆, and MoF₆," <u>Zeitschrift fur anorganische und allgemeine Chemie</u>. Band 196, 413-20 (1931).

^dN. S. Nikolaev and A. A. Opalovskii, "Solubility Isotherm at 0^o of the HF-MoF₆-H₂O System," <u>Russian J. Inorg. Chem. 4</u>, 532-6 (1959).

TABLE IV

Vapor Pressures of MoF₆

Solid	$\log P = \frac{-1823.1}{T} + 8.880^{a}$
Liquid	$\log P = \frac{-1394.9}{T} + 7.407^{a}$
	1400 0 h

Liquid
$$\log P = \frac{-1499.9}{T} + 7.766^{D}$$

Solid
$$\log P = \frac{-1722.9}{T} + 8.533^{b}$$

Solid -8.7 to $17.4^{\circ}C$ $\log P = \frac{-2166.5}{T} + 10.216^{b}$

Liquid

$$\log_{10} P_{mm} = -2047.15/T^{C} -4.28004 \log_{10} T + 20.19354$$

^aVon Otto Ruff and Ernst Ascher, "Einige Physikalische Konstanten von SiF₄, WF₆, and MoF₆," Zeitschrift fur anorganische und allgemeine Chemie. Band 196, 413-20 (1931).

^bGeorge H. Cady and George B. Hargreaves, "The Vapor Pressures of Some Heavy Transition-metal Hexafluorides," J. Chem. Soc. 1563-68 (1961).

^CDarrell W. Osborne, Felix Schreiver, John G. Malm. Henry Selig, and Leon Rochester, "Heat Capacity and Other Thermodynamic Properties of MoF₆ Between 4^o and 350^oK," J. Chem. Phys. 44, 2802-9 (1966).

Thermodynamic	Properties of MoF	6 For Change of	f State ^a
∆H _s	8.30	K cal/n	nole ^b
$\Delta H_{S}^{-8.70}C)$	7.850	**	с
∆H (<-8.7°C)	9.810	**	С
(△H _{van}) 8	11.1485	**	d
∆H _v	6.36	**	b
∆H _v	6.940	11	с
ΔH _v (298.15°K)	6.630 ± 0.025	11	d
∆H _f	1.059 ± 0.010	**	е
	0.920	1 8	С
$\Delta H_{f}^{(290.7^{\circ}K)}$	1.0342 ± 0.001	**	d
	1.957 ± 0.010	**	е
ΔH_t	1.960	**	С
$\Delta H_{+}(263.48^{\circ} K)$	1.9333 ± 0.002	11	d
ΔS_{v}	22.5	cal/deg/	'mole ^C
$\Delta S_{v}(298.15^{\circ}K)$	22.24 ± 0.08	*1	đ
∆s _f	3.15	*1	С
ΔS_{f}	3.65	**	f
ΔS_{f}	3.557 ± 0.10	11	đ
∆s ₊	7.40	**	с
ΔS_{t}	7.72	11	f
$a_{s} = sublimation$	$\mathbf{v} = \mathbf{v}$	vaporization	
f = fusion	t = ;	solid state tra	nsition
^D Von Otto Ruff a	nd Ernst Ascher, "	Einige Physikal	ische Kon-
stanten von SiF und allgemeine	$_4$, WF ₆ , and MoF ₆ ," Chemie. Band 196.	$\frac{\text{Zeitschrift fu}}{413-20}$ (1931)	r anorganische
^c George H. Cady	and George B. Harg	reaves. "The Va	nor Pressures
of Some Heavy T	ransition-metal He	xafluorides," J	<u>Chem</u> . Soc.,
1563-68 (1961). d			
and Leon Roches	e, Felix Schreiver ter. "Heat Capacity	, John G. Malm, v and Other The	Henry Selig, modynamic
Properties of M	oF_6 Between 4^0 and	350°K," <u>J</u> . <u>Che</u>	$\underline{\mathbf{m}}. \underline{\mathbf{Phys}}. \underline{44},$
2802-9 (1966). e. D. D. J. O.			
Properties of H	E. Myers and J. K. igher Fluorides. 1	. Clauss, "Ther . The Heat Capa	modynamic city, Entropy
and Heats of Tra	ansition of Molybde	enum Hexafluor	ide, and Nio-
fr. 1	ide," J. Phys. Cher	<u>n. 64</u> , 588-91 (1959).
Bernard Weinston cules," <u>Record</u> (ck, "Some Propertie Chem. Progress 23,	es of the Hexaf 23-50 (1962).	luoride Mole-

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TABLE	V
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TABLE VI

Thermodynamic Properties of MoF₆.

Formation Values.

∆H₀	(25°C,	gas)	-372.3 ± 0.2	К	cal/mole	ea
∆H	(25°C,	gas [*])	-382		**	b
∆H	(25°C,	liq.)	-388.6		**	b
∆H⁰	(25°C,	gas)	-370.2 ± 0.2	3	**	С
∆E ⁰	(25°C,	gas)	-371.1 ± 0.2		**	a
∆F ⁰	(25°C,	gas)	-350.8 ± 0.2		**	a
∆F	(25°C,	liq.)	-361.2		**	b
∆F ⁰	(25°C,	gas)	-351.9 ± 0.2	3	11	С
∆S⁰	(25°C,	gas)	- 72.13	cal	/deg/mo	le ^a
∆S⁰	(25°C,	gas)	$-68.41 \pm 0.$	19	11	С

*At vapor pressure of liquid.

^aJack L. Settle, Harold M. Feder and Ward N. Hubbard, "Fluorine Bomb Calorimetry. II. The Heat of Formation of Molybdenum Hexafluoride," J. Phys. Chem. 65, 1337-40 (1961).

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^bO. E. Myers and A. P. Brady, "Thermodynamic Properties of Higher Fluorides. 11. The Heats of Solution and of Formation of Molybdenum Hexafluoride, Tungsten Hexafluoride and Niobium Pentafluoride," J. Phys. Chem. 64, 591-4 (1960).

^CDarrell Osborne, Felix Schreiver, John G. Malm, Henry Selig, and Leon Rochester, "Heat Capacity and Other Themodynamic Properties of MoF₆ Between 4⁰ and 350⁰K," <u>J. Chem. Physics</u> <u>44</u>, 2802-9 (1966).

			TABI	LE VII				
		Norm	al Frequ (c	encies c cm ⁻¹)	of MoF ₆			
Ref.	a [*]	b	c,d	e,f	g	h,j	k	
v_1	741	736	741	.736	736	741	738.5	
ν ₂	643	641	645	641	641	643	643	
ν ₃	741	319	741	742	742	741	741.5	
V ₄	262	226*	260	269*	269	264	264.5	
ν ₅	312	619*	322	319	319	306	320.5	
ν ₆	122*	328*	234	240*	240	190	237	
*C	alcula	ted	*These f tent v	frequenci with calc	es are 1 rimetric	the most c values.	consis-	
^a Darr and Prop <u>44</u> , ^b K. N. Spect <u>Chem</u> . ^c T. G. Struc Spect ^d K. Ve	ell Os Leon Ro erties 2802-9 Tanner ra of M <u>Soc</u> . Burke, ture of ra," J.	sborne, F ochester, of MoF ₆ (1966). and A.B. Molybdenum 73, 1164- D. F. Su MoF ₆ , W <u>Chem. P</u> warln and	elix Sch "Heat C Between F. Dunca m and Tu 7 (1951) mith, and F ₆ , and hys. <u>20</u> , S. Sund	areiver, Capacity 4° and 3 an, "Rama angsten H '. d A. H. UF ₆ from 447-54 daram. "E	John G. and Othe 50°K," <u>d</u> n Effect (exafluor Nielsen, Infrare (1952).	Malm, He er Themod J. <u>Chem</u> . t and Ulf rides," <u>J</u> , "The Mo ed and Ra	enry Selig lynamic <u>Physics</u> traviolet <u>J. Am</u> . olecular aman cce Con-	,
stant Serie	s: Mo] s) <u>9</u> ,]	lecules o L74-9 (19	f the Ty 56).	pe XY ₆ ,"	\underline{Z} . Phys	\underline{S} . Chem.	(New	
^e J. Ga Some (1953	unt, "1 Group 6).	The Infra 5 Hexaflu	-red Spe orides,"	ectra and <u>Trans</u> .	Molecul Faraday	lar Struc <u>Soc</u> . 49,	ture of 1122-31	
¹ S. Su Therm <u>Chem</u> .	ndaram, odynami (New S	''Mean An Lc Proper Series) <u>3</u>	mplitude ties of $\frac{4}{2}$, 225-3	es of The Metal He 2 (1962)	rmal Vik xafluori	orations ides," <u>Z</u> .	and Phys.	
^g G. Na ages <u>Pure</u>	garajar of Chem Appl. I	n, "Mean nical Bone Phys. <u>4</u> ,	Amplitud ds: Oct 237-43 (les of Th ahedral (1966).	ermal Mo Hexafluo	otion and orides,"	l Shrink- <u>Indian</u> J.	
ⁿ Howar Spect	d H. Cl ra of M	laasen, Ho MoF ₆ and '	enry Sel TcF ₆ ," <u>J</u>	ig, and . <u>Chem</u> .	John G. Phys. <u>36</u>	Malm, "V 5, 2888-9	Vibrationa 0 (1962).	1
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TABLE VIII

Physical and Thermodynamic Properties of MoOF₄

97 ⁰ a,b
186.0 ⁰ , ^C 180 ^{a,b,d}
97.2° and 28.8mm°
White ^C
1020 cal/mole ^C
2.768 cal/mole/deg ^C
12,090 cal/mole ^C
13,100 cal/mole ^C
26.3 cal/mole/deg ^C

^aOtto Ruff and Fritz Eisner, "Uber die Darstellung und Eigenschaften von Fluoriden des Sechswertigen Molybdans," Berichte 40, 2926-35/(1907).

^bJ. Gaunt, "The Force Constants and Bond Lengths of Some Inorganic Hexafluorides," <u>Trans. Faraday Soc. 50</u>, 546-51 (1954).

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