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A LITERATURE SURVEY OF THE FLUORIDES
AND OXYFLUORIDES OF MOLYBDENUM

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A LITERATURE SURVEY OF THE FLUORIDES
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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. $\text{MoBr}_3 + 3\text{HF} \rightarrow \text{MoF}_3 + 3\text{HBr}$ at 600° in a Pt boat enclosed in a Cu tube.⁴
2. $2\text{Mo} + 6\text{HF} \xrightarrow[24 \text{ hrs}]{225^\circ\text{C}} 2\text{MoF}_3 + 3\text{H}_2$.⁵
3. $\text{MoF}_5 + \text{Mo} \rightarrow \text{MoF}_3$ at 400°C in a Ni capsule.⁶
4. $\text{MoF}_5 + \text{SbF}_3 \rightarrow \text{MoF}_3 + ?$. 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 MoF₃ 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, $a = 3.8985 \pm 0.005$) at <800°, has a distorted structure at >800°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 MoF₃ 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 R $\bar{3}$ c) determined by x-ray and neutron diffraction. Other workers (ref. 8) have confirmed that MoF₃ has a bimolecular rhombohedral unit cell with the R $\bar{3}$ c 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.

MoF₄

Reported methods for synthesis of MoF₄ are:

1. $2\text{Mo}(\text{CO})_6 + 3\text{F}_6 \xrightarrow{-75^\circ} 2\text{Mo}_2\text{F}_9 + 12\text{CO}; \text{Mo}_2\text{F}_9 \xrightarrow{170^\circ} \text{MoF}_4 + \text{MoF}_5$.⁹
2. Same as above except that the temperatures were -65° and 100°, respectively.¹⁰
3. $\text{Mo}(\text{CO})_6 + \text{MoF}_6 \rightarrow \text{MoF}_5 + \text{MoF}_4 + \text{CO}$; volatile products removed by vacuum.^{10,11}
4. $\text{MoF}_5 \xrightarrow{>150^\circ} \text{MoF}_6 + \text{MoF}_4$.^{10,11}

This compound has been described as light green,^{9,11} non-volatile,^{9,10,11} and immediately hydrolyzable with H₂O.⁹

Mo₂F₉

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: $4\text{Mo}(\text{CO})_6 + 9\text{F}_2 \xrightarrow{-65^\circ \text{ to } -75^\circ} 2\text{Mo}_2\text{F}_9 + 24\text{CO}$ and disproportionates by the reaction: $\text{Mo}_2\text{F}_9 \xrightarrow{100-170^\circ} \text{MoF}_4 + \text{MoF}_5$.

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 P₂O₅. The viscosity and high Trouton constant of MoF₅ are explained by assuming self ionization: $2\text{MoF}_5 \rightarrow \text{MoF}_4^+ + \text{MoF}_6^-$.² This compound has been synthesized by:

1. $\text{Mo}_2\text{F}_9 \xrightarrow{100-170^\circ} \text{MoF}_4 + \text{MoF}_5$.^{9,10}
2. $2\text{MoF}_6 + \text{PF}_3 \xrightarrow{\text{amb.}} 2\text{MoF}_5 + \text{PF}_5$.¹²⁻¹⁴
3. $\text{Mo} + \text{F}_2 \rightarrow \text{MoF}_6 + \text{"residue"}$, "residue" $\xrightarrow[\text{quartz}]{\text{distill}}$ MoF₅.^{6,11}
4. $\text{Mo}(\text{CO})_6 + \text{MoF}_6 \xrightarrow{250^\circ} \text{MoF}_5 + \text{MoF}_4 + \text{CO}$.^{10,11}
5. $\text{W}(\text{CO})_6 + \text{MoF}_6 \rightarrow \text{MoF}_5 + \text{WF}_4 + \text{CO}$.¹¹
6. $\text{Mo}(\text{CO})_6 + \text{F}_2 \xrightarrow{-65^\circ} \text{MoF}_5$.¹¹ + (?)
7. $\text{MoF}_6 + \text{Mo} \rightarrow \text{MoF}_5$.¹¹
8. $\text{WF}_4 + 2\text{MoF}_6 \xrightarrow{\text{amb.}} 2\text{MoF}_5 + \text{WF}_6$.¹³

MoF₅ disproportionates irreversibly (>150°) below its boiling point to form MoF₄ and MoF₆.^{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 $a = 9.61 \pm 0.01\text{\AA}$, $b = 14.22 \pm 0.02\text{\AA}$, $c = 5.16 \pm 0.01\text{\AA}$, and $\beta = 94^\circ 21' \pm 20'$.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 MMoF₆¹⁵ (M = Na, K, Rb, Cs) were formed by: $2\text{MoF}_6 + 2\text{MI} \xrightarrow{-60^\circ} \text{I}_2 + 2\text{MMoF}_6$ 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 $a = 8.20, 5.11, \text{ and } 5.29\text{\AA}$, respectively. The K compound is tetragonal with $a = 10.17$ and $c = 9.97\text{\AA}$.¹⁵ The Mo-F distance in NaMoF₆ is $1.74 \pm 0.03\text{\AA}$.¹¹ The Na compound has been further studied (ref. 16) and found to be face centered cubic, space group Fm3m (O_h⁵, No. 255). All of the interatomic distances are listed in this report.

K₂MoOF₅

The compound K₂MoOF₅ has been reported¹⁵ to be a readily hydrolyzed pale green solid.

MoF₆

Molybdenum hexafluoride has been synthesized by:

1. $\text{F}_2 + \text{Mo} \xrightarrow{60-400^\circ} \text{MoF}_6$ ^{4,10,12,17-21} in Pt boat in Ni or Cu. F₂ diluted with N₂.
2. $\text{Mo} + \text{BrF}_3 \rightarrow \text{MoF}_6 + ?$.²²
3. $\text{Mo} + \text{ClF}_3 \rightarrow \text{MoF}_6 + ?$ in Ni boat.²⁰
4. $\text{MoCl}_5 + \text{HF} \rightarrow \text{MoF}_6 + ?$.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: $\text{CrF}_5 > \text{UF}_6 > \text{MoF}_6 > \text{WF}_6$. 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 $1.83\text{\AA}$,²⁹⁻³¹ $1.840\text{\AA}$,²⁷ $1.830\text{\AA}$,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 ($\times 10^{-5}$ dynes/cm). The physical, structural, and thermal properties of MoF_6 are summarized in Tables II-VII. Traces of the Raman,^{19,25,27} infrared,^{19,24,27} ultraviolet,²⁵ and nuclear magnetic resonance³⁷ spectra of MoF_6 have been reported.

The values of Cp^0 , S^0 , $\text{H}^0 - \text{H}_0^0$, $-(\text{F}^0 - \text{H}_0^0)/\text{T}$ for gaseous MoF_6 in the ideal state have been calculated from the fundamental frequencies over the temperature range 50 - 1600°K and are tabulated in references 21, 24, 27, 31, and 38.

The values of Cp determined calorimetrically for solid and liquid MoF_6 from 50 to 298.5°K are tabulated in reference 39. The enthalpy and entropy of gaseous MoF_6 from 400 to 2000°K are tabulated⁴⁰ and summarized as $\text{H}_\text{T} - \text{H}_{298.15} = 35.80\text{T} + 0.59 \times 10^{-3}\text{T}^2 + 6.97 \times 10^5\text{T}^{-1} - 13,064$ (298 - 2000°K , gas)⁴⁰ and $\text{Cp} = 35.80 + 1.18 \times 10^{-3}\text{T} - 6.97 \times 10^5\text{T}^{-2}$.⁴⁰ The functions Cp^0 , S^0 , $\text{H}^0 - \text{H}_0^0$, $-(\text{F}^0 - \text{H}_0^0)/\text{T}$ are also tabulated in reference 21 for solid 5 - 290.70°K , liquid 290.76 - 350°K , and gas 50 - 1000°K . 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 MoF_6 - UF_6

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

M_2MoF_8

The family of compounds M_2MoF_8 ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$) has been reported.²² The authors of reference 22 tried but failed to synthesize the sodium analog.

MoOF₄

The compound MoOF₄^{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:

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

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

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

MoO₂F₂

The compound MoO₂F₂^{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:

<u>Material</u>	<u>Reference</u>
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 valves 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

M. P.	64 ⁰ , ^{a, b} 67 ^c
B. P.	213.6 ⁰ , ^d 211 ^c
T. P.	67.0 ⁰ , pressure very low ^d
$\Delta H_{\text{vaporization}}$	12,370 cal/mole ^d
$\Delta S_{\text{vaporization}}$	25.4 cal/mole/deg. ^d
Vapor pressure	~2mm (at 65 ⁰) ^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. Am. Chem. Soc. 82, 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. Chem. Soc., 1568-74 (1961).

TABLE II

Thermal and Structural Properties of MoF ₆	
M. P.	17, ^a 17.4, ^{b-d} 17.5, ^e 17.4±0.5°C ^f
B. P.	35, ^{a,c,g} 34.0°C ^h
T. P.	17.5°C & 406.5mm, ^{c,g} 17.4 & 398.1mm
Solid-Solid Transition	-9.6, ^{e,d} -8 _f ° & 104.7mm, ^h -9.8±0.5
High Temperature Form	bcc a = 6.23Å ^{0f,i}
Low Temperature Form at -20°C	orthorhomic ^{f,i} a = 9.65±.02Å b = 8.68±.03Å c = 5.05±.02Å

^aOtto Ruff and Fritz Eisner, "Über 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).

^fL. E. Trevorow, 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 Physikalische Konstanten von SiF₄, WF₆, and MoF₆," Zeitschrift für anorganische 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).

ⁱDarrell Osborne, Felix Schreiver, John G. Malm, Henry Selig, and Leon Rochester, "Heat Capacity and Other Thermodynamic Properties of MoF₆ Between 4° and 350°K," J. Chem. Physics 44, 2802-9 (1966).

TABLE III
Density of MoF₆

Density, High Temp. Solid	8°C	2.91 g/cc (measured) ^a
" " " "	0°C	2.88 " "
" " " "	10°C	2.88 " (x-ray)
" " " "	278°C	2.88 ± 0.04 (x-ray) ^b
" Low " "	237°C	3.27 ± 0.03 "
" Liquid	17.5°C ^c	2.551 g/cm ³
" "	19°C	2.543 "
" "	27°C	2.503 "
" "	34°C	2.470 "
" "	17.4°C ^d	2.551 "
d(Low Temp. Solid) for 77.16 to 237°C	= 3.619 - 0.00130T (g/cm ³) ^b	
d(High Temp. Solid)	= 3.464 - 0.00210T (g/cm ³) ^b	
d(Liquid) for 294.33 to 344.63°C	= 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 Schreiber, John G. Malm, Henry Selig and Leon Rochester, "Heat Capacity and Other Thermodynamic Properties of MoF₆ Between 4° and 350°C," J. Chem. Physics 44, 2802-9 (1966).

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

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

TABLE IV
Vapor Pressures of MoF₆

Solid	$\log P = \frac{-1823.1}{T} + 8.880^a$
Liquid	$\log P = \frac{-1394.9}{T} + 7.407^a$
Liquid	$\log P = \frac{-1499.9}{T} + 7.766^b$
	17.4 to 34°C
Solid	$\log P = \frac{-1722.9}{T} + 8.533^b$
	-8.7 to 17.4°C
Solid	$\log P = \frac{-2166.5}{T} + 10.216^b$
	-60 to -8.7°C
Liquid	$\log_{10} P_{\text{mm}} = \frac{-2047.15}{T} + 4.28004 \log_{10} T + 20.19354^c$

^aVon Otto Ruff and Ernst Ascher, "Einige Physikalische Konstanten von SiF₄, WF₆, and MoF₆," Zeitschrift für 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° and 350°K," J. Chem. Phys. 44, 2802-9 (1966).

TABLE V

Thermodynamic Properties of MoF₆ For Change of State^a

ΔH_s	8.30	K cal/mole ^b	
$\Delta H_s (>-8.7^\circ\text{C})$	7.850	"	c
$\Delta H_s (<-8.7^\circ\text{C})$	9.810	"	c
$(\Delta H_{\text{vap}})^\circ$	11.1485	"	d
ΔH_v	6.36	"	b
ΔH_v	6.940	"	c
$\Delta H_v (298.15^\circ\text{K})$	6.630 $\pm$ 0.025	"	d
ΔH_f	1.059 $\pm$ 0.010	"	e
ΔH_f	0.920	"	c
$\Delta H_f (290.7^\circ\text{K})$	1.0342 $\pm$ 0.001	"	d
ΔH_t	1.957 $\pm$ 0.010	"	e
ΔH_t	1.960	"	c
$\Delta H_t (263.48^\circ\text{K})$	1.9333 $\pm$ 0.002	"	d
ΔS_v	22.5	cal/deg/mole ^c	
$\Delta S_v (298.15^\circ\text{K})$	22.24 $\pm$ 0.08	"	d
ΔS_f	3.15	"	c
ΔS_f	3.65	"	f
ΔS_f	3.557 $\pm$ 0.10	"	d
ΔS_t	7.40	"	c
ΔS_t	7.72	"	f

^as = sublimation

v = vaporization

f = fusion

t = solid state transition

^bVon Otto Ruff and Ernst Ascher, "Einige Physikalische Konstanten von SiF₄, WF₆, and MoF₆," Zeitschrift für anorganische und allgemeine Chemie. Band 196, 413-20 (1931).^cGeorge H. Cady and George B. Hargreaves, "The Vapor Pressures of Some Heavy Transition-metal Hexafluorides," J. Chem. Soc., 1563-68 (1961).^dDarrell Osborne, Felix Schreiber, John G. Malm, Henry Selig, and Leon Rochester, "Heat Capacity and Other Thermodynamic Properties of MoF₆ Between 4° and 350°K," J. Chem. Phys. 44, 2802-9 (1966).^eA. P. Brady, O. E. Myers and J. K. Clauss, "Thermodynamic Properties of Higher Fluorides. 1. The Heat Capacity, Entropy, and Heats of Transition of Molybdenum Hexafluoride, and Niobium Pentafluoride," J. Phys. Chem. 64, 588-91 (1959).^fBernard Weinstock, "Some Properties of the Hexafluoride Molecules," Record Chem. Progress 23, 23-50 (1962).

TABLE VI
Thermodynamic Properties of MoF₆.
Formation Values.

ΔH^0 (25°C, gas)	-372.3 ± 0.2	K cal/mole ^a
ΔH (25°C, gas*)	-382	" ^b
ΔH (25°C, liq.)	-388.6	" ^b
ΔH^0 (25°C, gas)	-370.2 ± 0.23	" ^c
ΔE^0 (25°C, gas)	-371.1 ± 0.2	" ^a
ΔF^0 (25°C, gas)	-350.8 ± 0.2	" ^a
ΔF (25°C, liq.)	-361.2	" ^b
ΔF^0 (25°C, gas)	-351.9 ± 0.23	" ^c
ΔS^0 (25°C, gas)	- 72.13	cal/deg/mole ^a
ΔS^0 (25°C, gas)	$- 68.41 \pm 0.19$	" ^c

*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).

^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 Thermodynamic Properties of MoF₆ Between 4° and 350°K," J. Chem. Physics 44, 2802-9 (1966).

TABLE VII
Normal Frequencies of MoF₆
(cm⁻¹)

Ref.	a [*]	b	c,d	e,f	g	h,j	k
ν_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
ν_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

*Calculated

*These frequencies are the most consistent with calorimetric values.

^aDarrell Osborne, Felix Schreiver, John G. Malm, Henry Selig, and Leon Rochester, "Heat Capacity and Other Thermodynamic Properties of MoF₆ Between 4° and 350°K," J. Chem. Physics 44, 2802-9 (1966).

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TABLE VIII

Physical and Thermodynamic Properties of MoOF_4

M. P.	97° ^{a, b}
B. P.	186.0° , ^c 180° ^{a, b, d}
T. P.	97.2° and 28.8mm ^c
Color	White ^c
ΔH fusion	1020 cal/mole ^c
ΔS fusion	$2.768 \text{ cal/mole/deg}$ ^c
ΔH vaporization	$12,090 \text{ cal/mole}$ ^c
ΔH sublimation	$13,100 \text{ cal/mole}$ ^c
ΔS vaporization	$26.3 \text{ cal/mole/deg}$ ^c

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