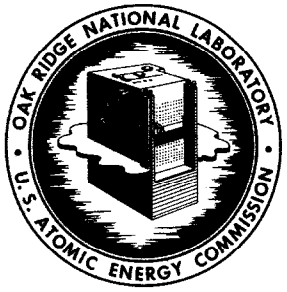

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
NUCLEAR DIVISION
for the
U.S. ATOMIC ENERGY COMMISSION

ORNL - TM - 1976

A LITERATURE SURVEY OF THE FLUORIDES AND OXYFLUORIDES OF MOLYBDENUM

C. F. Weaver
H. A. Friedman

ORNL-TM-1976

Contract No. W-7405-eng-26

REACTOR CHEMISTRY DIVISION

A LITERATURE SURVEY OF THE FLUORIDES AND OXYFLUORIDES OF MOLYBDENUM

C. F. Weaver and H. A. Friedman

OCTOBER 1967

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

fcy

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.

MoF_3

Reported methods for the synthesis of MoF_3 are:

1. $MoBr_3 + 3HF \rightarrow MoF_3 + 3HBr$ at 600^0 in a Pt boat enclosed in a Cu tube.[4]
2. $2Mo + 6HF \xrightarrow[24\ hrs]{225^0C} 2MoF_3 + 3H_2$.[5]
3. $MoF_5 + Mo \rightarrow MoF_3$ at 400^0C in a Ni capsule.[6]
4. $MoF_5 + SbF_3 \rightarrow MoF_3 + ?$. The SbF_3 was carried in a stream of A at 150 to 200^0C.[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 "MoF_3" 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 ReO_3 and TaF_3 (cubic, space group Pm3m, a = 3.8985 ± 0.005) at <800°, has a distorted structure at >800°[7] and is reduced by H_2 to Mo metal.[4] The material produced by method (2) was found to be cubic by x-ray analysis[5] and is probably the same as the product of method (1).

Properties reported[6] 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 VF_3 type structure (space group $R\bar{3}c$) determined by x-ray and neutron diffraction. Other workers (ref. 8) have confirmed that MoF_3 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.

MoF_4

Reported methods for synthesis of MoF_4 are:

1. $2Mo(CO)_6 + 3F_6 \xrightarrow{-75^0} 2Mo_2F_9 + 12CO$; $Mo_2F_9 \xrightarrow{170^0} MoF_4 + MoF_5$.[9]
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. $MoF_5 \xrightarrow{>150^0} MoF_6 + MoF_4$.[10,11]

This compound has been described as light green,[9,11] non-volatile,[9,10,11] and immediately hydrolyzable with H_2O.[9]

Mo_2F_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: $4Mo(CO)_6 + 9F_2 \xrightarrow{-65 \text{ to } -75^0} 2Mo_2F_9 + 24CO$ and disproportionates by the reaction: $Mo_2F_9 \xrightarrow{100-170^0} MoF_4 + MoF_5$.

MoF_5

MoF_5 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 P_2O_5. The viscosity and high Trouton constant of MoF_5 are explained by assuming self ionization: $2MoF_5 \rightarrow MoF_4^+ + MoF_6^-$.[2] This compound has been synthesized by:

1. $Mo_2F_9 \xrightarrow{100-170^0} MoF_4 + MoF_5$.[9,10]
2. $2MoF_6 + PF_3 \xrightarrow{amb.} 2MoF_5 + PF_5$.[12-14]
3. $Mo + F_2 \rightarrow MoF_6$ + "residue", "residue" $\xrightarrow[quartz]{distill} MoF_5$.[6,11]
4. $Mo(CO)_6 + MoF_6 \xrightarrow{25^0} MoF_5 + MoF_4 + CO$.[10,11]
5. $W(CO)_6 + MoF_6 \rightarrow MoF_5 + WF_4 + CO$.[11]
6. $Mo(CO)_6 + F_2 \xrightarrow{-65^0} MoF_5$[11] + (?)
7. $MoF_6 + Mo \rightarrow MoF_5$.[11]
8. $WF_4 + 2MoF_6 \xrightarrow{amb.} 2MoF_5 + WF_6$.[13]

MoF_5 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 MoF_5. MoF_5 dissolves in MoF_6 to form a yellow solution.[12] It is monoclinic (space group C2m) with $a = 9.61 \pm 0.01$Å, $b = 14.22 \pm 0.02$Å, $c = 5.16 \pm 0.01$Å, and $\beta = 94^0\ 21' \pm 20'$.[11] An electron density projection on the 001 plane and a table of interatomic distances may also be found in reference 11. MoF_5 will reduce UF_6 to UF_5 in excess UF_6 and to UF_4 in excess MoF_5.[14]

$MMoF_6$

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. $KMoF_6$ 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 $NaMoF_6$ 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 (O_h^5, No. 255). All of the interatomic distances are listed in this report.

K_2MoOF_5

The compound K_2MoOF_5 has been reported[15] to be a readily hydrolyzed pale green solid.

MoF_6

Molybdenum hexafluoride has been synthesized by:

1. $F_2 + Mo \xrightarrow{60\text{-}400^0} MoF_6$[4,10,12,17-21] in Pt boat in Ni or Cu. F_2 diluted with N_2.
2. $Mo + BrF_3 \rightarrow MoF_6 + ?$.[22]
3. $Mo + ClF_3 \rightarrow MoF_6 + ?$ in Ni boat.[20]
4. $MoCl_5 + HF \rightarrow MoF_6 + ?$.[20]

The MoF_6 is purified by trap to trap distillation over NaF.[12,17,23] The reactivity of MoF_6 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 molecules[24-27] with d^2sp^3 hybrid bonds, has a bond strength of 105Kcal/mole[13,28] and has a second virial coefficient of -923 cm^3/mole.[21]

The Mo-F bond has a reported length of 1.83Å,[29-31] 1.840Å,[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 MoF_6 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 MoF_6 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°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 tabulated[40] and summarized as $H_T - H_{298.15} = 35.80T + 0.59 \times 10^{-3}T^2 + 6.97 \times 10^5 T^{-1} - 13{,}064$ (298-2000°K, gas)[40] and $Cp = 35.80 + 1.18 \times 10^{-3}T - 6.97 \times 10^5 T^{-2}$.[40] The functions Cp^0, S^0, $H^0 - H_0^0$, $-(F^0 - H_0^0)/T$ 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 (M = K, Rb, Cs) has been reported.[22] The authors of reference 22 tried but failed to synthesize the sodium analog.

$MoOF_4$

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_2F_2

The compound MoO_2F_2[33,42] sublimes with decomposition at ~270°C[42] 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 MoF_6 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 MoF_5

M. P.	64°,[a,b] 67°[c]
B. P.	213.6°,[d] 211°[c]
T. P.	67.0°, pressure very low[d]
$\Delta H_{vaporization}$	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]

[a]R. D. Peacock, "Two New Fluorides of Molybdenum," Proc. Chem. Soc., 59 (1957).

[b]D. 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).

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

[d]George 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] -8.7 & 104.7mm,[h] -9.8±0.5[f]
High Temperature Form	bcc a = 6.23Å[f,i]
Low Temperature Form at -20°C	orthorhomic[f,i] a = 9.65±.02Å b = 8.68±.03Å c = 5.05±.02Å

[a]Otto Ruff and Fritz Eisner, "Uber die Darstellung und Eigenschaften von Fluoriden des Sechswertigen Molybdans," Berichte 40, 2926-35 (1907).

[b]T. A. O'Donnell, "The Preparation and Manipulation of Molybdenum Hexafluoride," J. Chem. Soc., 4681-2 (1956).

[c]N. S. Nikolaev and A. A. Opalovskii, "Solubility Isotherm at 0° of the HF-MoF_6-H_2O System," Russian J. Inorg. Chem. 4, 532-6 (1959).

[d]Bernard Weinstock, "Some Properties of the Hexafluoride Molecules," Record Chem. Progress 23, 23-50 (1962).

[e]A. 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.

[g]Von Otto Ruff and Ernst Ascher, "Einige Physikalsiche Konstanten von SiF_4, WF_6, and MoF_6," Zeitschrift fur anorganische und allgemeine Chemie. Band 196, 413-20 (1931).

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

[i]Darrell Osborne, Felix Schreiver, John G. Malm, Henry Selig, and Leon Rochester, "Heat Capacity and Other Thermodynamic Properties of MoF_6 Between 4° and 350°K," J. Chem. Physics 44, 2802-9 (1966).

TABLE III

Density of MoF_6

Density, High Temp. Solid	8°C	2.91 g/cc (measured)[a]	
" " " "	0°C	2.88 "	"
" " " "	10°C	2.88 "	(x-ray)
" " " "	278°K	2.88 ± 0.04	(x-ray)[b]
" Low " "	237°K	3.27 ± 0.03	"
" Liquid	17.5°C [c]	2.551 g/cm³	
" "	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°K = 3.619 - 0.00 130T (g/cm³)[b]

d(High Temp. Solid) = 3.464 - 0.00210T (g/cm³)[b]

d(Liquid) for 294.33 to 344.63°K = 3.733 - 0.00404T (g/cm³)[b]

[a] 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 and Uranium Hexafluoride," ANL-7240, August 1966.

[b] Darrell Osborne, Felix Schreiver, John G. Malm, Henry Selig and Leon Rochester, "Heat Capacity and Other Thermodynamic Properties of MoF_6 Between 4° and 350°K," J. Chem. Physics 44, 2802-9 (1966).

[c] Von Otto Ruff and Ernst Ascher, "Einige Physikalische Konstanten von SiF_4, WF_6, and MoF_6," Zeitschrift fur anorganische und allgemeine Chemie. Band 196, 413-20 (1931).

[d] N. S. Nikolaev and A. A. Opalovskii, "Solubility Isotherm at 0° of the $HF-MoF_6-H_2O$ System," Russian J. Inorg. Chem. 4, 532-6 (1959).

TABLE IV

Vapor Pressures of MoF_6

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	$\log_{10} P_{mm} = -2047.15/T$[c] $-4.28004 \log_{10} T + 20.19354$

[a]Von Otto Ruff and Ernst Ascher, "Einige Physikalische Konstanten von SiF_4, WF_6, and MoF_6," Zeitschrift fur anorganische und allgemeine Chemie. Band 196, 413-20 (1931).

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

[c]Darrell W. Osborne, Felix Schreiver, John G. Malm. Henry Selig, and Leon Rochester, "Heat Capacity and Other Thermodynamic Properties of MoF_6 Between 4° and 350°K," J. Chem. Phys. 44, 2802-9 (1966).

TABLE V

Thermodynamic Properties of MoF_6 For Change of State[a]

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

[a] s = sublimation v = vaporization
f = fusion t = solid state transition

[b] Von Otto Ruff and Ernst Ascher, "Einige Physikalische Konstanten von SiF_4, WF_6, and MoF_6," Zeitschrift fur anorganische und allgemeine Chemie. Band 196, 413-20 (1931).

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

[d] Darrell Osborne, Felix Schreiver, John G. Malm, Henry Selig, and Leon Rochester, "Heat Capacity and Other Themodynamic Properties of MoF_6 Between 4° and 350°K," J. Chem. Phys. 44, 2802-9 (1966).

[e] A. 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).

[f] Bernard Weinstock, "Some Properties of the Hexafluoride Molecules," Record Chem. Progress 23, 23-50 (1962).

TABLE VI

Thermodynamic Properties of MoF_6.

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 ± 0.19	"	c

*At vapor pressure of liquid.

[a]Jack 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).

[b]O. 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).

[c]Darrell Osborne, Felix Schreiver, John G. Malm, Henry Selig, and Leon Rochester, "Heat Capacity and Other Themodynamic Properties of MoF_6 Between 4° and 350°K," J. Chem. Physics 44, 2802-9 (1966).

TABLE VII

Normal Frequencies of MoF_6 (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.

[a]Darrell Osborne, Felix Schreiver, John G. Malm, Henry Selig, and Leon Rochester, "Heat Capacity and Other Themodynamic Properties of MoF_6 Between 4^0 and 350^0K," J. Chem. Physics 44, 2802-9 (1966).

[b]K. N.Tanner and A.B.F. Duncan, "Raman Effect and Ultraviolet Spectra of Molybdenum and Tungsten Hexafluorides," J. Am. Chem. Soc. 73, 1164-7 (1951).

[c]T. G. Burke, D. F. Smith, and A. H. Nielsen, "The Molecular Structure of MoF_6, WF_6, and UF_6 from Infrared and Raman Spectra," J. Chem. Phys. 20, 447-54 (1952).

[d]K. Venkateswarln and S. Sundaram, "Evaluation of Force Constants: Molecules of the Type XY_6," Z. Phys. Chem. (New Series) 9, 174-9 (1956).

[e]J. Gaunt, "The Infra-red Spectra and Molecular Structure of Some Group 6 Hexafluorides," Trans. Faraday Soc. 49, 1122-31 (1953).

[f]S. Sundaram, "Mean Amplitudes of Thermal Vibrations and Thermodynamic Properties of Metal Hexafluorides," Z. Phys. Chem. (New Series) 34, 225-32 (1962).

[g]G. Nagarajan, "Mean Amplitudes of Thermal Motion and Shrinkages of Chemical Bonds: Octahedral Hexafluorides," Indian J. Pure Appl. Phys. 4, 237-43 (1966).

[h]Howard H. Claasen, Henry Selig, and John G. Malm, "Vibrational Spectra of MoF_6 and TcF_6," J. Chem. Phys. 36, 2888-90 (1962).

[j]G. Nagarajan, "Potential Constants for the Hexafluorides of Molybdenum and Rhenium," Aust. J. Chem. 16, 906-7 (1963).

[k]C.W.F.T. Pistorius, "Potential Field and Force Constants of Octahedral Molecules," J. Chem. Phys. 29, 1328-32 (1958).

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 cal/mole/deg[c]
ΔH vaporization	12,090 cal/mole[c]
ΔH sublimation	13,100 cal/mole[c]
ΔS vaporization	26.3 cal/mole/deg[c]

[a]Otto Ruff and Fritz Eisner, "Uber die Darstellung und Eigenschaften von Fluoriden des Sechswertigen Molybdans," Berichte 40, 2926-35 (1907).

[b]J. Gaunt, "The Force Constants and Bond Lengths of Some Inorganic Hexafluorides," Trans. Faraday Soc. 50, 546-51 (1954).

[c]George 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).

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

References

1. W. R. Grimes, "Chemical Research and Development for Molten-Salt Breeder Reactors," ORNL-TM-1853, June 6, 1967, pp. 61-81.

2. S. S. Kirslis, F. F. Blankenship, and C. F. Baes, Jr., Reactor Chemistry Division Annual Progress Report, January 31, 1967, ORNL-4076, pp. 48-53.

3. S. S. Kirslis and F. F. Blankenship, MSR Program Semiannual Progress Report, February 28, 1967, ORNL-4119, pp. 124-143.

4. H. J. Emeleus and V. Gutmann, "Studies on the Fluorides of Molybdenum and Vanadium," J. Chem. Soc., 2979-82 (1949).

5. E. L. Muetterties and J. E. Castle, "Reactions of Hydrogen Fluoride with Metals and Metalloids," J. Inorg. and Nucl. Chem. 18, 148-53 (1961).

6. D. 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).

7. V. Gutmann and K. H. Jack, "The Crystal Structures of Molybdenum Trifluoride, MoF_3, and Tantalum Trifluoride, TaF_3," Acta Cryst. 4, 244-46 (1951).

8. M. K. Wilkinson, E. O. Wollan, H. R. Child, and J. W. Cable, "Neutron Diffraction Investigation of Magnetic Ordering in the Trifluorides of 4-d-transition Elements," Phys. Rev. 121, 74-7 (1961).

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

10. George 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).

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

12. T. A. O'Donnell and D. F. Stewart, "Chemical Reactions of Molybdenum Hexafluoride," J. Inorg. and Nucl. Chem. 24,309-14 (1962).

13. T. A. O'Donnell and D. F. Stewart, "Reactivity of Transition Metal Fluorides. 1. Higher Fluorides of Chromium, Molybdenum, and Tungsten," Inorg. Chem. 5, 1434-7 (1966).

14. T. A. O'Donnell and D. F. Stewart, "Reactivity of Transition Metal Fluorides. Uranium Hexafluoride," Inorg. Chem. 5, 1438-41 (1966).

15. G. B. Hargreaves and R. D. Peacock, "Some Fluoromolybdates (V) and Fluorotungstates (V)," J. Chem. Soc. 4212-4 (1957).

16. A. J. Edwards and R. D. Peacock, "The Structure of Sodium Hexafluoromolybdate (V)," J. Chem. Soc., 4253-4 (1961).

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

18. T. A. O'Donnell, The Preparation and Manipulation of Molybdenum Hexafluoride," J. Chem. Soc., 4681-2 (1956).

19. T. G. Burke, D. F. Smith, and A. H. Nielsen, "The Molecular Structure of MoF_6, WF_6, and UF_6 from Infrared and Raman Spectra," J. Chem. Phys. 20, 447-54 (1952).

20. N. S. Nikolaev and A. A. Opalovskii, "Solubility Isotherm at 0^0 of the HF-MoF_6-H_2O System," Russian J. Inorg. Chem. 4, 532-6 (1959).

21. Darrell Osborne, Felix Schreiver, John G. Malm, Henry Selig, and Leon Rochester, "Heat Capacity and Other Thermodynamic Properties of MoF_6 Between 4^0 and 350^0K," J. Chem. Phys. 44, 2802-9 (1966).

22. B. Cox, D.W.A. Sharp, and A. G. Sharpe, "Complex, Part V. Complexes Formed by Molybdenum Hexafluoride, Tungsten Hexafluoride, and Rhodium Tetrafluoride," J. Chem. Soc. 1243-4 (1956).

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

24. J. Gaunt, "The Infra-red Spectra and Molecular Structure of Some Group 6 Hexafluorides," Trans. Faraday Soc. 49, 1122-31 (1953).

25. K. N. Tanner and A.B.F. Duncan, "Raman Effect and Ultraviolet Spectra of Molybdenum and Tungsten Hexafluorides," J. Am. Chem. Soc. 73, 1164-7 (1951).

26. Verner Schomaker and Roy Glauber, "The Born Approximation in Electron Diffraction," Nature 170, 290-1 (1952).

27. Howard H. Claasen, Henry Selig, and John G. Malm, "Vibrational Spectra of MoF_6 and TcF_6," J. Chem. Phys. 36, 2888-90 (1962).

28. J. H. Canterford and T. A. O'Donnell, "Reactivity of Transition Metal Fluorides. 111. Higher Fluorides of Vanadium, Niobium, and Tantalum," Inorg. Chem. 5, 1442-46 (1966).

29. G. Nagarajan, "Mean Amplitudes of Thermal Motion and Shrinkages of Chemical Bonds: Octahedral Hexafluorides," Indian J. Pure Appl. Phys. 4, 237-43 (1966).

30. J. Gaunt, "The Force Constants and Bond Lengths of Some Inorganic Hexafluorides," Trans. Faraday Soc. 50, 546-51 (1954).

31. S. Sundaran, "Mean Amplitudes of Thermal Vibrations and Thermodynamic Properties of Metal Hexafluorides," Z. Phys. Chem. (New Series) 34, 225-32 (1962).

32. E. Meisingseth and S. J. Cyvin, "Mean Amplitude of Vibration and Bastiansen-Monino Shrinkage Effects in Some Octahedral XY_6 Molecules," Acta Chem. Scand. 16, 2452-5 (1962).

33. Howard H. Claassen, "Force Constants of Metal Hexafluorides," J. Chem. Phys. 30, 968-72 (1959).

34. C.W.F.T. Pistorius, "Potential Field and Force Constants of Octahedral Molecules," J. Chem. Phys. 29, 1328-32 (1958).

35. G. Nagarajan, "Potential Field and Force Constants of Some Octahedral XY_6 Type Molecules," Bull. Soc. Chim. Belg. 72, 276-85 (1963).

36. G. Nagarajan, "Potential Constants for the Hexafluorides of Molybdenum and Rhenium," Aust. J. Chem. 16, 906-7 (1963).

37. E. L. Muetterties and W. D. Phillips, "Structure and Exchange Processes in Some Inorganic Fluorides by Nuclear Magnetic Resonance," J. Am. Chem. Soc. 81, 1084-8 (1959).

38. G. Nagarajan, "Thermodynamic Properties of Some Metal Hexafluorides," Bull. Soc. Chim. Belg. 71, 77-81 (1962).

39. A. 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).

40. K. K. Kelley, "Bureau of Mines Bulletin 584," p. 126, 1960.

41. 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.

42. Otto Ruff and Fritz Eisner, "Uber die Darstellung und Eigenschaften von Fluoriden des sechswertigen Molybdans," Berichte 40, 2926-35 (1907).

ORNL-TM-1976

INTERNAL DISTRIBUTION

1. R. K. Adams
2. G. M. Adamson
3. R. G. Affel
4. L. G. Alexander
5. R. F. Apple
6. C. F. Baes
7. J. M. Baker
8. S. J. Ball
9. H. F. Bauman
10. S. E. Beall
11. M. Bender
12. C. E. Bettis
13. E. S. Bettis
14. F. F. Blankenship
15. R. E. Blanco
16. J. O. Blomeke
17. R. Blumberg
18. E. G. Bohlmann
19. C. J. Borkowski
20. C. E. Boyd
21. J. Braunstein
22. M. A. Bredig
23. R. B. Briggs
24. H. R. Bronstein
25. G. D. Brunton
26. D. A. Canonico
27. S. Cantor
28. W. L. Carter
29. G. I. Cathers
30. J. M Chandler
31. C. W. Collines
32. E. L. Compere
33. W. H. Cook
34. L. T. Corbin
35. J. L. Crowley
36. F. L. Culler, Jr.
37. J. M. Dale
38. D. G. Davis
39. R. J. DeBakker
40. S. J. Ditto
41. A. S. Dworkin
42. D. A. Dyslin
43. J. R. Engel
44. E. P. Epler
45. D. E. Ferguson
46. L. M. Ferris
47. A. P. Fraas
48. H. A. Friedman
49. J. H. Frye, Jr.
50. C. H. Gabbard
51. R. B. Gallaher
52. H. E. Goeller
53. W. R. Grimes
54. A. G. Grindell
55. R. H. Guymon
56. B. A. Hannaford
57. P. H. Harley
58. D. G. Harman
59. C. S. Harrill
60. P. N. Haubenreich
61. P. G. Hendon
62. D. N. Hess
63. J. R. Hightower
64. M. R. Hill
65. H. W. Hoffman
66. R. W. Horton
67. T. L. Hudson
68. H. Inouye
69. W. H. Jordan
70. P. R. Kasten
71. R. J. Kedl
72. M. T. Kelley
73. M. J. Kelly
74. C. R. Kennedy
75. T. W. Kerlin
76. H. T. Kerr
77. S. S. Kirslis
78. H. W. Kohn
79. A. I. Krakoviak
80. J. W. Krewson
81. C. E. Lamb
82. J. A. Lane
83. R. B. Lindauer
84. A. P. Litman
85. G. H. Llewellyn
86. M. I. Lundin
87. R. N. Lyon
88. H. G. MacPherson
89. R. E. MacPherson
90. C. D. Martin
91 C. E. Mathews
92. T. H. Mauney

93. H. McClain
94. R. W. McClung
95. H. E. McCoy
96. H. F. McDuffie
97. C. K. McGlothlan
98. C. J. McHargue
99. L. E. McNeese
100. A. S. Meyer
101. R. R. Minue
102. R. L. Moore
103. D. M. Moulton
104. H. A. Nelms
105. J. P. Nichols
106. E. L. Nicholson
107. L. C. Oakes
108. P. Patriarca
109. A. M. Perry
110. T. W. Pickel
111. H. B. Piper
112. B. E. Prince
113. J. L. Redford
114. J. D. Redman
115. M. Richardson
116. R. C. Robertson
117. G. D. Robbins
118. W. C. Robinson
119. H. C. Roller
120. K. A. Romberger
121-122. M. W. Rosenthal
123. H. C. Savage
124. C. E. Schilling
125. Dunlap Scott
126. J. L. Scott
127. H. E. Seagren
128. C. E. Sessions
129. W. F. Schaffer
130. J. H. Shaffer
131. C. S. Sherer
132. M. J. Skinner
133. G. M. Slaughter
134. A. N. Smith
135. F. J. Smith
136. G. P. Smith
137. O. L. Smith
138. P. G. Smith
139. I. Spiewak
140. R. C. Steffy
141. W. C. Stoddart
142. H. H. Stone
143. R. A. Strehlow
144. J. R. Tallackson
145. E. H. Taylor
146. W. Terry
147. R. E. Thoma
148. L. M. Toth
149. D. B. Trauger
150. J. S. Watson
151. H. L. Watts
152. C. F. Weaver
153. B. H. Webster
154. A. M. Weinberg
155. J. R. Weir
156. W. J. Werner
157. K. W. West
158. M. E. Whatley
159. J. C. White
160. L. V. Wilson
161. G. Young
162. H. C. Young
163. F. C. Zapp
164-165. Central Research Library
166. Document Reference Section
167-169. Laboratory Records Dept.
170. Laboratory Records, ORNL R.C.
171. ORNL Patent Office
172-186. Division of Technical Information Extension
187. Laboratory and University Division

EXTERNAL DISTRIBUTION

188-190. D. F. Cope, AEC, ORO
191. A. Giambusso, AEC, Washington, D. C.
192. W. J. Larkin, AEC, ORO
193. C. L. Matthews, AEC, ORO
194-195. T. W. McIntosh, AEC, Washington, D. C.
196. H. M. Roth, AEC, ORO
197. M. Shaw, AEC, Washington, D. C.
198. W. L. Smalley, AEC, ORO