MASTER

ORNL-3088
UC-4 - Chemistry

MEASUREMENT OF DISSOCIATION
PRESSURE OF MOLYBDENUM
FLUORIDE-SODIUM FLUORIDE COMPLEX

F. R. Groves, Jr.

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in USA. Price \$0.50. Available from the

Office of Technical Services
Department of Commerce
Washington 25, D.C.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Unit Operations Section

Measurement of Dissociation Pressure of Molybdenum
Fluoride--Sodium Fluoride Complex

F. R. Groves, Jr.

DATE ISSUED

APR 11 1951

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

ABSTRACT

The dynamic (gas saturation) method was used to determine upper and lower limits for the dissociation pressure of the complex formed when MoF_6 is absorbed by NaF . The limits were 0.4 to 4.6 mm Hg at 100°C and 8.4 to 27 mm Hg at 150°C . A lower limit, 64 mm Hg, was determined at 200°C . As a check on the method the dissociation pressure of the complex $\text{UF}_6 \cdot (\text{NaF})_3$ was determined at 100, 200, and 240°C . The measured values were in satisfactory agreement with accepted values of dissociation pressure for this compound.

CONTENTS

	<u>Page</u>
1.0 INTRODUCTION	4
2.0 DYNAMIC METHOD FOR MEASURING DISSOCIATION PRESSURE	4
2.1 Lower Limit for Dissociation Pressure	4
2.2 Upper Limit for Dissociation Pressure	6
3.0 DESCRIPTION OF EQUIPMENT	8
4.0 DESCRIPTION OF WORK AND RESULTS	12
4.1 Dissociation Pressure Measurements with Fluorine as Carrier Gas	12
4.2 Dissociation Pressure Measurements with Nitrogen as Carrier Gas	13
4.3 Dissociation Pressure of $\text{UF}_6 \cdot (\text{NaF})_3$	14
4.4 Preparation of Fluoride Complexes	14
5.0 REFERENCES	15

1.0 INTRODUCTION

The purpose of this study was to determine the limits on dissociation pressure of $\text{MoF}_6 \cdot (\text{NaF})_x$, which should be useful for suggesting the best operating temperatures for Volatility Pilot Plant absorbers. One stage of the volatility process for nuclear fuel processing involves purification of UF_6 by absorption on a bed of NaF pellets. The UF_6 forms the complex $\text{UF}_6 \cdot (\text{NaF})_3$ and is held by the absorber bed. Some of the impurities (fission product and corrosion product fluorides) are not held at the absorber operating temperature. The UF_6 is subsequently desorbed by heating and collected in cold traps. Some of the sorbed impurities are not desorbed and are thus separated from the UF_6 .

As a working hypothesis we assumed that the fission product fluorides form complexes with NaF analogous to $\text{UF}_6 \cdot (\text{NaF})_3$. The specific object of the study was to demonstrate a method for measuring the dissociation pressure of such complexes. Molybdenum hexafluoride (MoF_6 , bp 35°C) was selected for study because it is easy to prepare and can be handled readily as a gas at moderate temperatures.

The $\text{MoF}_6 \cdot (\text{NaF})_x$ work should be extended by studying the effects of saturator bed length and carrier gas flow rate. This should narrow the spread between upper and lower limits on dissociation pressure and indicate which limit is closer to the true dissociation pressure.

The author gratefully acknowledges the assistance received from members of the Unit Operations Section of the Chemical Technology Division, particularly L. E. McNeese, J. Beams, F. N. McLain, and T. D. Napier.

2.0 DYNAMIC METHOD FOR MEASURING DISSOCIATION PRESSURE

The dynamic method¹ was selected for measurement of dissociation pressure. Its chief advantages are low cost and simplicity of the equipment and technique involved. Two variations of the method were used: one provided a lower limit for dissociation pressure, the other an upper limit.

2.1 Lower Limit for Dissociation Pressure

An inert carrier gas is metered into a bed of $\text{MoF}_6 \cdot (\text{NaF})_x$ complex whose dissociation pressure is to be measured. As the carrier gas passes through the bed, MoF_6 is desorbed into it. If the bed is long enough and the rate of desorption is fast enough, the carrier gas will emerge in equilibrium with the bed, and the partial pressure of MoF_6 in the gas will equal the dissociation pressure of the complex (Fig. 1).

The loss in weight of the bed of complex gives the moles, m , of MoF_6 removed by the metered quantity, G moles, of carrier gas passed through the system. The total pressure, P , at the bed outlet is measured by means of a manometer. Then, assuming ideal gas behavior, the partial pressure, p_1 , of MoF_6 in the gas leaving the bed is given by

$$p_1 = \left(\frac{m}{G+m} \right) P$$

UNCLASSIFIED
ORNL-LR-DWG 51338

Fig. 1. Method of determining lower limit for dissociation pressure of $\text{MoF}_6 \cdot (\text{NaF})_x$.

The assumption of ideal gas behavior for MoF_6 is satisfactory near atmospheric pressure.²

As noted above, if the bed of complex is long enough or the desorption rate fast enough, the calculated partial pressure will equal the dissociation pressure of the complex at the temperature of the bed. If the desorption rate is too slow, equilibrium will not be attained between gas stream and bed. The calculated partial pressure of MoF_6 will then represent a lower limit for the dissociation pressure of the complex.

2.2 Upper Limit for Dissociation Pressure

In this variation two beds of complex—a presaturator and a saturator—are used (Fig. 2). The presaturator filled with complex is held at a temperature T_1 , perhaps 50°C higher than the temperature, T_2 , of the saturator, which is filled with pure NaF . A carrier gas is metered through the system.

The presaturator serves mainly as a source of MoF_6 . As the carrier gas passes through it, MoF_6 is desorbed into the gas. If the temperature T_1 of the presaturator is high enough, the partial pressure of MoF_6 in the gas leaving it will be greater than the dissociation pressure of the complex at the temperature T_2 of the saturator (Fig. 2). Thus when the gas enters the saturator MoF_6 will be absorbed by the NaF to form the complex. If the bed is long enough or the absorption rate is fast enough, the partial pressure of MoF_6 in the gas leaving the saturator will equal the dissociation pressure of the complex at temperature T_2 . If the absorption rate is too slow this partial pressure will represent an upper limit for the dissociation pressure of the complex. The partial pressure of MoF_6 in the gas leaving the saturator can be obtained from the formula

$$p_n = \left(\frac{S-W}{S-W+G} \right) P$$

where p_n = partial pressure of MoF_6 leaving saturator, mm Hg

P = total pressure of gas leaving saturator, mm Hg

S = weight of presaturator, g moles MoF_6

W = weight gain of saturator, g moles MoF_6

G = metered quantity of carrier gas passed through, g moles

In this variation the presaturator behaves in the same way as the bed of complex in the method described above for determining the lower limit for the dissociation pressure. Thus, the partial pressure of MoF_6 in the gas stream leaving the presaturator can be obtained from

$$p_1 = \left(\frac{S}{S+G} \right) P$$

Fig. 2. Method of determining upper limit for dissociation pressure of $\text{MoF}_6 \cdot (\text{NaF})_x$.

when p_1 = partial pressure of MoF_6 in gas leaving presaturator, mm Hg

S = weight loss of presaturator, g moles MoF_6

G = metered quantity of carrier gas passed through, g moles

P = total pressure of gas leaving presaturator, mm Hg

This partial pressure represents a lower limit for the dissociation pressure of the complex at the temperature, T_1 , of the presaturator.

3.0 DESCRIPTION OF EQUIPMENT

In determining the dissociation pressure (Fig. 3) the carrier gas was metered through a capillary flowmeter. The meter consisted of a type 347 stainless steel capillary 5 ft long, 20 mils i.d., and 20 mils wall thickness. A pressure gauge was placed upstream from the capillary, and downstream was a pressure gauge followed by a Monel Hoke valve for flow control. The flow control valve was adjusted to maintain a constant pressure difference across the capillary, yielding a constant flow rate through it. Two carrier gases—nitrogen and fluorine—were used in these experiments. For both gases the downstream pressure gauge was a brass-trim 0-30 psig gauge. For nitrogen metering a pressure regulator with a similar gauge was used upstream. For fluorine a DP cell actuating a pressure gauge in the fluorine supply system was used to indicate upstream pressure.

The capillary was calibrated with nitrogen by the soap bubble method. The meter maintained a constant flow rate within 2% over a period of 3 hr. No trend was apparent in the flow rate measured over this period. The calibration for fluorine was calculated from the nitrogen calibration. Calculation of the Reynolds number indicated a laminar flow in the capillary. To obtain the fluorine calibration the nitrogen calibration at a given pressure drop was multiplied by the ratio of nitrogen viscosity to fluorine viscosity at the capillary temperature.

The preheater was made from 3 ft of 1/4-in.-dia copper tubing wound into a 3-in.-dia coil. The preheater was wrapped with 36 ft of 20 gauge Nichrome resistance wire and covered with a layer of asbestos tape. This arrangement provided 500 watts of heating capacity at 110 volts.

Four copper vessels (6, 7, 8, 9 in Fig. 3) were provided for containing the beds of NaF and complex. These vessels were made from 3/4-in. copper tubing (Fig. 4). To facilitate accurate weighing, the beds of NaF or complex were held in Monel carrying tubes (Fig. 5) which fit inside the copper vessels. The carrying tubes were made from 3/8-in. Monel pipe turned down to fit inside the copper vessels. The lower ends of the carrying tubes were closed with Monel screen welded into place. The upper ends were threaded so that they could be screwed into the upper closure of the copper vessels, which were tapped to receive them. The carrying tubes were made in two sizes: 6 in. and 12 in. overall length. The 6-in. tubes weighed about 50 g empty, the 12-in. tubes 100 g.

UNCLASSIFIED
ORNL-LR-DWG 51335 R1

- 1 Pressure regulator, 0-30 psig.
- 2 Type 347 stainless steel capillary, 5 ft long, 20 mils i.d., 20 mils wall thickness.
- 3 Pressure gauge, 0-30 psig.
- 4 Valve, Monel, Hoke.
- 5 Preheater.
- 6 Presaturator.
- 7 Saturator.
- 8,9 Absorbers.
- 10 Chemical trap, soda lime.

Fig. 3. Apparatus for dynamic method of dissociation pressure measurement.

Fig. 4. Fluorinator or absorber vessel.

UNCLASSIFIED
ORNL-LR-DWG 51340

Fig. 5. Monel carrying tube, 12 in.

The first two saturator tubes (6 and 7 of Fig. 3) were heated by clamshell heaters (220 watts, 110 volts). The last two copper vessels (8 and 9 of Fig. 3) were each wound with 36 ft of 20-gauge Nichrome resistance wire and covered with asbestos tape. This provided 500 watts at 110 volts. All connecting tubing between vessels was 1/4-in.-dia copper wound with 20-gauge Nichrome wire. The heaters were manually controlled with variacs. Temperatures of the vessels were measured by copper-constantan thermocouples held in place on the outer surface of the vessels by asbestos tape.

A chemical trap containing 4200 g of 4 to 8 mesh soda lime removed fluorine from the gases leaving the equipment.

4.0 DESCRIPTION OF WORK AND RESULTS

The complex $\text{MoF}_6 \cdot (\text{NaF})_x$ was loaded into 6-in.-dia carrier tubes, weighed on the analytical balance, and placed in the first pair (vessels 6 and 7 of Fig. 3) of copper saturators. Carrier gas (~ 110 cc/min) was metered through the system for 2 hr while the saturators were held at the temperature given. The carrying tubes filled with complex were weighed at the end of the run, and the loss in weight was used to compute a lower limit for the dissociation pressure of $\text{MoF}_6 \cdot (\text{NaF})_x$.

Because of the corrosive nature of fluorine, nitrogen was used as carrier gas for the first experiments, but the MoF_6 decomposed and results were not reproducible. With fluorine as the carrier gas no decomposition was noted and corrosion was not prohibitive. Fluorine carrier was therefore used for determining reliable dissociation pressure limit values.

4.1 Dissociation Pressure Measurements with Fluorine as Carrier Gas

When measurements were made with fluorine no color change in the pellets of complex occurred after several hours exposure at 150°C , and the experimental results were reproducible, indicating no MoF_6 decompositions (Table 1). Upper and lower limits were then determined for the dissociation pressure of the complex $\text{MoF}_6 \cdot (\text{NaF})_x$ at several temperatures. The spread between the upper and lower limits indicated that equilibrium between complex and carrier gas was not attained in either the desorption (lower limit) or absorption (upper limit) part of the experiments. The approach to equilibrium in the presaturators and saturators could be improved by varying the saturator bed length or the flow rate of carrier gas through the beds.

To account for the corrosion by fluorides, the Monel carrying tubes were weighed empty before and after each run and a series of blank runs in which no complex (only NaF) was present was made. Corrosion of the Monel tubes generally amounted to 0 to 7 mg gain or loss in weight and could be estimated accurately in each run by weighing the carrying tubes empty. The blank runs showed an appreciable change in weight of the NaF even when no complex was present. The NaF in vessel 6 (Fig. 3) generally lost weight at 150°C while the NaF in the other vessels gained. The weight change was greatest for the downstream vessels (7, 8, and 9). The loss

Table 1. Dissociation Pressure Limits of $\text{MoF}_6 \cdot (\text{NaF})_x$

Run No.	Temp, °C	MoF ₆ conc, g/g NaF	Dissociation Pressure Limit, mm Hg	
			Lower	Upper
Fluorine Carrier Gas				
3	100	0.333	0.4	--
4	100	0.331	0.3	--
6	100	--	--	4.6
6	150	0.313	8.5	--
7	150	0.287	8.4	--
8	150	--	--	27.0
8	200	--	64.0	--
Nitrogen Carrier Gas				
1	150	0.14	4.6	--
2	150	0.12	1.9	--

in vessel 6 suggested an attack by fluorine on some impurity in the NaF. The gain in weight downstream suggested that volatile corrosion products from the copper tubing were being carried downstream and deposited on the NaF there. Both these possibilities should be studied in further experiments. For the present, the corrosion difficulties were met by avoiding use of the downstream vessels (8 and 9 of Fig. 3) where weight changes due to corrosion were large and by running a blank after each experimental measurement to estimate weight changes due to corrosion in vessels 6 and 7. Corrosion corrections depended on temperature, duration of run, and condition of the equipment. A typical weight loss for a 12-in. bed (~ 27 g) of NaF pellets exposed in vessel 1 for 2 hr at 150°C was 0.025 g. A typical weight gain for a 12-in. bed exposed in vessel 7 for 2 hr at 150°C was 0.06 g.

4.2 Dissociation Pressure Measurements with Nitrogen as Carrier Gas

With nitrogen as the carrier gas the calculated dissociation pressures could not be reproduced in duplicate runs, but appeared to decrease as the quantity of MoF₆ held on the NaF pellets decreased (Table 1). The color of the complex changed from pure white to a deep bluish-purple after exposure to nitrogen at 150°C for 2 hr, indicating that some chemical reaction other

than simple desorption was occurring. A study of the literature on the chemistry of MoF_6 indicated that it is easily reduced in the presence of certain metals (copper, iron) or traces of organic matter to a lower fluoride or mixture of fluorides.³ The exact composition of the reduction product is not known, but its color is invariably deep blue or purple.

The apparent decrease in dissociation pressure as the quantity of absorbed MoF_6 decreased might have been caused by this reduction reaction or by failure to attain equilibrium between carrier gas and complex in the saturators. The rate of desorption of MoF_6 from the complex should decrease with time. At first the desorbed MoF_6 comes mainly from the surface of the NaF pellet. As time passes the MoF_6 must diffuse from the interior of the pellet to the surface before being desorbed, and the rate of desorption would decline. Thus as the amount of MoF_6 on the pellets decreases the bed becomes less efficient in saturating the carrier gas. The calculated dissociation pressure would therefore decline.

Similar measurements with the complex $\text{NbF}_5 \cdot (\text{NaF})_x$ showed a decrease in calculated dissociation pressure with decrease in NbF_5 content of the pellets (Table 2). No color change was observed in the complex.

Table 2. Lower Limit for Dissociation Pressure of $\text{NbF}_5 \cdot (\text{NaF})_x$ at 150°C (Nitrogen Carrier Gas)

Run No.	NbF_5 Conc, g/g NaF	Lower Limit for Dissociation Pressure, mm Hg
1	0.092	0.66
2	0.086	0.39
3	0.084	0.28

4.3 Dissociation Pressure of $\text{UF}_6 \cdot (\text{NaF})_3$

The good agreement between accepted values⁴ of the dissociation pressure of $\text{UF}_6 \cdot (\text{NaF})_3$ and those measured by our technique indicates the validity of our technique for measuring dissociation pressures of such complexes (Table 3). The lower limits determined by our method appeared to be closer to the accepted values than the upper limits.

4.4 Preparation of Fluoride Complexes

The fluorides of molybdenum (MoF_6) and niobium (NbF_5) used in the studies were prepared by direct reaction of the elements (Table 4). These fluorides are volatile and quite sensitive to moisture. Since the fluoride complex with NaF was the compound to be studied, it was decided to prepare it immediately without isolating and purifying the fluoride itself.

Table 3. Dissociation Pressure of $\text{UF}_6 \cdot (\text{NaF})_3$
(Fluorine Carrier Gas)

Run No.	Temp, °C	Dissociation Pressure, mm Hg		
		Lower Limit	Upper Limit	Accepted Value ^a
2	100	--	0.7	1×10^{-2}
2	200	1.6	--	1.6
3	200	--	3.4	1.6
3	240	8.5	--	9.0

^a Reference 4.

Table 4. Preparation of Fluoride Complexes

Run No.	Fluoride	Wt. of Metal Used, g	Wt. of Fluoride Absorbed on NaF, g	Fraction of Stoichiometric Yield Absorbed, %
2	MoF_6	5.72	10.3	82
3	MoF_6	10.5	19.2	84
4	MoF_6	10.0	15.5	71
1	NbF_5	2.06	3.3	80

Fluoride was metered through a capillary into the fluorinator, which was heated by a clamshell heater (Fig. 6). The fluorinator vessel had the same construction as the copper vessels for holding NaF beds (Fig. 4) and held metallic molybdenum (200 mesh, 99.8%). The molybdenum in the fluorinator was preheated at 150°C. As soon as fluorine was admitted the temperature rose rapidly, indicating that the fluorination reaction was proceeding. The temperature was kept below 300°C by controlling the fluorine flow rate. The MoF_6 produced was swept by the fluorine to the absorbers, which were copper vessels of the sort described already. They held carrying tubes filled with NaF pellets to form the complex.

NbF_5 was prepared by the same technique.

5.0 REFERENCES

1. F. H. Cushman and F. Daniels, "Outlines of Physical Chemistry," p. 153, 7th ed., John Wiley and Sons, New York, 1945.

UNCLASSIFIED
ORNL-LR-DWG 51334 R1

- 1 Type 347 stainless steel capillary, 5 ft long, 20 mils i.d., 20 mils wall thickness.
- 2 Gauge, brass trim, 0 - 30 psig.
- 3 Monel valve, Hoke.
- 4 Fluorinator vessel, copper.
- 5 Absorber, copper.
- 6 Absorber, copper.
- 7 Chemical trap, soda lime.

Fig. 6. Equipment for preparation of MoF₆.

2. J. Kleinbert, W. J. Argersinger, Jr., and F. Greswald, "Inorganic Chemistry," p. 519, D. C. Heath and Co., Boston, 1960.
3. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 11, 610, Longmans, Green and Co., London, 1943.
4. G. I. Cathers, M. R. Bennet, and R. L. Jolley, "Formation and Decomposition Reactions of the Complex $UF_6 \cdot (NaF)_3$," ORNL-CF-57-4-25.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ORNL-3088
UC-4 - Chemistry
TID-4500 (16th ed.)

INTERNAL DISTRIBUTION

1. Biology Library	61. S. C. Lind
2. Health Physics Library	62. R. B. Lindauer
3-4. Central Research Library	63. A. P. Litman
5. Reactor Division Library	64. J. T. Long
6. ORNL - Y-12 Technical Library,
Document Reference Section	65. R. J. McNamee
7-26. Laboratory Records Department	66. L. E. McNeese
27. Laboratory Records, ORNL R.C.	67. R. P. Milford
28. E. D. Arnold	68. E. C. Moncrief
29. R. E. Blanco	69. K. Z. Morgan
30. G. E. Boyd	70. J. P. Murray (K-25)
31. J. C. Bresee	71. M. L. Nelson
32. K. B. Brown	72. D. Phillips
33. F. R. Bruce	73. W. W. Pitt, Jr.
34. W. H. Carr	74. P. M. Reyling
35. G. I. Cathers	75. A. D. Ryon
36. C. E. Center	76. H. E. Seagren
37. R. A. Charpie	77. E. D. Shipley
38. R. S. Cockreham	78. M. J. Skinner
39-40. F. L. Culler	79. A. H. Snell
41. W. K. Eister	80. S. H. Stainker
42. D. E. Ferguson	81. J. C. Suddath
43. J. H. Frye, Jr.	82. J. A. Swartout
44. H. E. Goeller	83. E. H. Taylor
45. A. T. Gresky	84. J. W. Ullmann
46. F. R. Groves, Jr.	85. W. E. Unger
47. C. E. Guthrie	86. C. D. Watson
48. P. A. Haas	87. A. M. Weinberg
49. C. W. Hancher	88. M. E. Whatley
50. C. S. Harrill	89. C. E. Winters
51. A. Hollaender	90. R. G. Wymer
52. R. W. Horton	91. E. L. Youngblood
53. A. S. Householder	92. J. W. Youngblood
54. R. G. Jordan (Y-12)	93. D. L. Katz (consultant)
55. W. H. Jordan	94. C. E. Larson (consultant)
56. C. P. Keim	95. I. Perlman (consultant)
57. M. T. Kelley	96. J. H. Rushton (consultant)
58. E. Lamb	97. H. Worthington (consultant)
59. J. A. Lane	98. T. H. Pigford (consultant)
60. T. A. Lincoln	

EXTERNAL DISTRIBUTION

99. Division of Research and Development, AEC, ORO
100-691. Given distribution as shown in TID-4500 (16th ed.) under Chemistry
category (75 copies - OTS)