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Preparation of $MF_6 \cdot NaF$ Complexes with Uranium, Tungsten, and Molybdenum Hexafluorides[1]

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The hexafluorides of uranium, tungsten, and molybdenum react with sodium fluoride to reach 1:2 and 1:1 stoichiometric ratios with unexpected speed when the sodium fluoride has been formed by decomposition of $UF_6 \cdot 2NaF$. The equilibrium pressures of the newly prepared 1:1 complexes for the reaction $2(MF_6 \cdot NaF) \rightleftarrows MF_6 + MF_6 \cdot 2NaF$ are: for UF_6, $\log P_{mm} = 11.06 \pm 0.02 - (3.48 \times 10^3)/T$; for WF_6, $\log P_{mm} = 7.05 \pm 0.02 + (1.99 \times 10^3)/T$; for MoF_6, $\log P_{mm} = 7.29 \pm 0.03 - (1.83 \times 10^3)/T$.

Introduction

This report describes the preparation by gas–solid reactions, of solid complexes of sodium fluoride with uranium hexafluoride, tungsten hexafluoride, and molybdenum hexafluoride of the formula type $MF_6 \cdot NaF$ and the measurement of the equilibrium pressures of the metal hexafluorides over these complexes. An improved preparation of compounds of the type $MF_6 \cdot 2NaF$, previously reported,[2] is also presented.

For the previously reported[2] preparation of $UF_6 \cdot 2NaF$, $WF_6 \cdot 2NaF$, and $MoF_6 \cdot 2NaF$, the metal hexafluoride was sorbed upon a sodium fluoride prepared by decomposing $NaF \cdot 4HF$. Metal hexafluoride in excess of that needed to form the $MF_6 \cdot 2NaF$ compound sorbed slowly and incompletely even at lower temperatures. A subsequent observation that metal hexafluorides sorbed better upon sodium fluoride formed by decomposing $UF_6 \cdot 2NaF$ led to the work reported here.

The compound $UF_6 \cdot NaF$ has already been prepared by Malm and Selig[3] by reaction of uranium hexafluoride with sodium fluoride suspended in fluorocarbon (C_7F_{16}). They report a decomposition pressure of about 35 mm at 100° (in agreement with data presented here). The similar compounds $CsUF_7$, $CsWF_7$, $CsMoF_7$, NH_4UF_7, NH_4WF_7, and NH_4MoF_7 have also been reported.[4,5]

Experimental Section

Materials and Gasometric Apparatus.—These are as described previously.[2]

Preparation of the Sodium Fluoride Complexes with Hexafluorides of Uranium, Tungsten, and Molybdenum.—The procedures are as described previously[2] except for the preparation of the sodium fluoride sorbent and the temperatures at which the sorptions were conducted.

The sodium fluoride sorbent was prepared by either of two methods, which differed in the manner of the preliminary formation of the complex $UF_6 \cdot 2NaF$ which was to be subsequently decomposed. The first method for preparing the preliminary $UF_6 \cdot 2NaF$ was by uranium hexafluoride sorption after hydrogen fluoride treatment of the sodium fluoride, as described previously.[2] The second method for preparing the preliminary $UF_6 \cdot 2NaF$ consisted in successive sorption–desorption cycles of uranium hexafluoride on 270-mesh sodium fluoride without any prior hydrogen fluoride treatment. The uranium hexafluoride sorption curves for each of these preparative methods are shown in Figure 1; the first method was preferred because it was faster and required fewer manipulations. The preliminary $UF_6 \cdot 2NaF$, thus prepared, was then decomposed by heating to 350° at low pressure to remove gaseous uranium hexafluoride while leaving the solid relic of the former solid complex; a final treatment of the residue with fluorine at 200 mm and at 350° removed traces of uranium. Surprisingly, the surface area of sodium fluoride so prepared was little different from that made by hydrogen fluoride treatment alone.[2]

The critical importance of temperature of sorption, noted in the previous work,[2] for preparation of the $MF_6 \cdot 2NaF$ compounds no longer prevailed with the sodium fluoride made by the improved technique; the sorptions proceeded very rapidly at all temperatures tested, provided that the gas pressure exceeded the decomposition pressure of the compound formed. In the upper section of Figure 2 are presented comparisons of the previously reported sorptions,[2] each at the optimum temperature, with sorptions at 150° for each of the metal hexafluorides using the improved sodium fluoride. In the lower section of Figure 2 are shown the sorption curves for the preparation at temperatures of 60 to 80° of the $MF_6 \cdot NaF$ complexes discussed here. These complexes may be prepared in two steps, using successively lower temperatures, or in one step at the lower temperature. Two-step sorptions, using different metal hexafluorides at each step, were successful where uranium or tungsten hexafluoride was the second gas; the temperatures and curve forms were similar to those shown in Figure 2 for those gases.

Results

Gasometric and Chemical Analyses.—The gasometric ratios NaF/MF_6 shown in Figure 2 are (previous results[1] given in parentheses for comparison)

Hexafluoride	Ratio after first step	Ratio after second step
UF_6	2.00 (2.01)	1.00
WF_6	2.00 (2.11)	1.04
MoF_6	2.01 (2.24)	1.05

The concentrations of uranium, tungsten, and molybdenum found in the final product compare with the theoretical values as

	% U in $UF_6 \cdot NaF$	% W in $WF_6 \cdot NaF$	% Mo in $MoF_6 \cdot NaF$
Found	58.9	52.1	35.1
Theoretical	60.4	54.1	38.1

As in the previous work,[2] the metal contents are systematically low because of nickel impurity introduced from the sample tray and because of water pickup; the

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] S. Katz, *Inorg. Chem.*, **3**, 1598 (1964).

[3] J. G. Malm, H. Selig, and S. Siegel, *ibid.*, **5**, 130 (1966).

[4] N. S. Nikolaev and V. F. Sukhoverkhov, *Dokl. Akad. Nauk SSSR*, **136**, 621 (1961).

[5] B. Volavsek, *Croat. Chem. Acta*, **33**, 181 (1961).

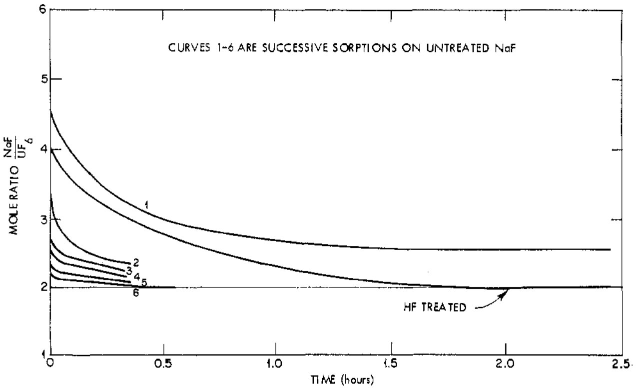

Figure 1.—Sorption of UF_6 on HF-treated and on untreated NaF to prepare $UF_6 \cdot 2NaF$.

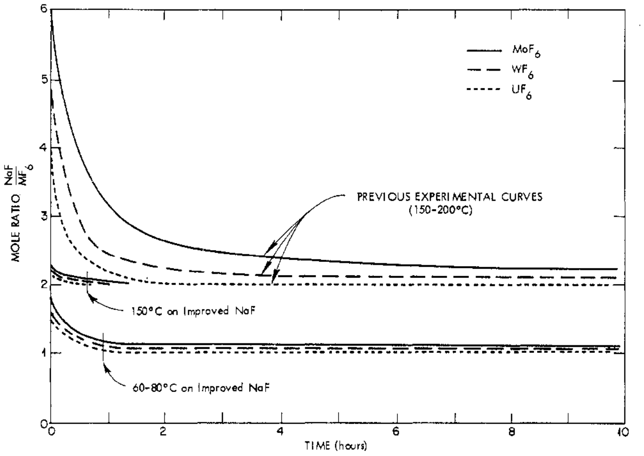

Figure 2.—Comparisons of MF_6 sorptions by previous and new techniques to obtain $MF_6 \cdot 2NaF$ and completion of sorption to obtain $MF_6 \cdot NaF$.

bias is slightly larger here because the fluorine treatment was more rigorous (causing more nickel metal to be converted to the fluoride), and the product more readily reacted with atmospheric moisture.

Equilibrium Pressures of the $MF_6 \cdot NaF$ Complexes.—The equilibrium pressures, measured as described,[2] and the corresponding solid compositions and temperatures are presented in Tables I–III and are plotted in Figure 3 in the conventional way, log P_{mm} *vs.* $1/T$, along with the straight line fitted by the least-squares method. The equations for the lines and the calculated enthalpy changes (kcal/mole of evolved gas), assuming no substantial solid solutions, are

$$\log P_{mm} = 11.06 \pm 0.02 - (3.48 \times 10^3)/T;$$
$$\Delta H = 15.9 \pm 0.2 \quad (UF_6 \text{ over } UF_6 \cdot NaF)$$

$$\log P_{mm} = 7.05 \pm 0.02 - (1.99 \times 10^3)/T;$$
$$\Delta H = 9.1 \pm 0.2 \quad (WF_6 \text{ over } WF_6 \cdot NaF)$$

$$\log P_{mm} = 7.29 \pm 0.03 - (1.83 \times 10^3)/T;$$
$$\Delta H = 8.4 \pm 0.4 \quad (MoF_6 \text{ over } MoF_6 \cdot NaF)$$

for the reaction $2(MF_6 \cdot NaF) \leftrightharpoons MF_6 + MF_6 \cdot 2NaF$.

TABLE I

UF_6 PRESSURES OVER $UF_6 \cdot 2NaF$–$UF_6 \cdot NaF$ SOLID PHASES

Temp, °C	Solid composition,[a] mole ratio NaF/UF_6	Press of UF_6, mm
69	1.008	8
78	1.009	13
83	1.013	18
83	1.026	20
98	1.038	50
99.5	1.082	52.5
110	1.072	92
114	1.093	114
121	1.266	166
121.5	1.269	170
123	1.443	180
123.5	1.185	188
124	1.192	194
125	1.385	192

[a] By gas evolution measurements assuming $UF_6 \cdot NaF$ as initial solid.

TABLE II

WF_6 PRESSURES OVER $WF_6 \cdot 2NaF$–$WF_6 \cdot NaF$ SOLID PHASES

Temp, °C	Solid composition,[a] mole ratio NaF/WF_6	Press of WF_6, mm
67	1.761	16
67.5	1.718	17
83	1.037	27
96	1.026	41
109	1.074	68
123.5	1.916	105
137	1.675	156
137	1.387	160
139	1.115	163
139	1.401	171

[a] By gas evolution measurements assuming $WF_6 \cdot NaF$ as initial solid.

TABLE III

MoF_6 PRESSURES OVER $MoF_6 \cdot 2NaF$–$MoF_6 \cdot NaF$ SOLID PHASES

Temp, °C	Solid composition,[a] mole ratio NaF/MoF_6	Press of MoF_6, mm
45	1.026	34
54	1.039	51
72	1.076	93
73	1.165	94
74	1.277	98
75	1.304	120
90	1.368	178

[a] By gas evolution measurements assuming $MoF_6 \cdot NaF$ as initial solid.

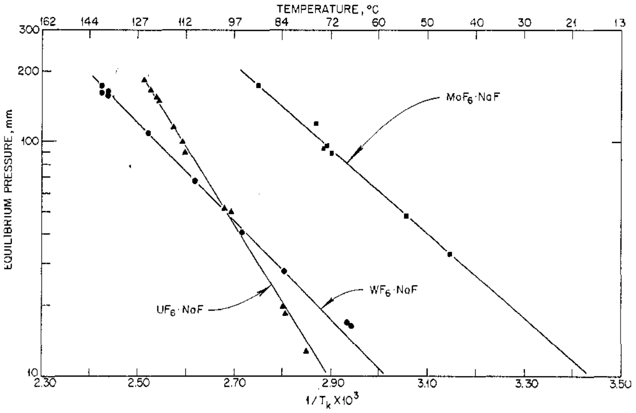

Figure 3.—Equilibrium pressures of MF_6 over $MF_6 \cdot 2NaF$–$MF_6 \cdot NaF$.

Evidence for Absence of Solid Solutions.—The data of the preceding section demonstrate the interdependence of system temperature and MF_6 gas pressure independently of solid composition for solid compositions both close in composition to $MF_6 \cdot NaF$ (mole ratios less than 1.03) and different (see Tables I–III). A similar condition was evidenced in the previous paper[2] for the system $MF_6 \cdot 2NaF$.

Also, the MF_6 pressure over the stoichiometric composition ($MF_6 \cdot NaF$) was raised isothermally (at a temperature where the equilibrium pressure over the $MF_6 \cdot NaF$–$MF_6 \cdot 2NaF$ pair is less than 1 mm) to 200 mm without altering the solid composition as measured by gas inventory changes.

Furthermore, the temperature of the system containing the stoichiometric composition ($MF_6 \cdot NaF$) was decreased in the presence of 200 mm of MF_6 without altering the solid composition; the solid composition remained unchanged during the subsequent temperature rise in the presence of less than 1 mm of MF_6. For these tests the temperature was cycled through the complete interval permitted by vapor pressures of liquid MF_6 and equilibrium pressures of the $MF_6 \cdot NaF$–$MF_6 \cdot 2NaF$ pairs (approximately 50° interval).

Equilibrium Pressures of Mixtures of $MF_6 \cdot NaF$ Complexes.—The equilibrium pressure data for the mixture of $UF_6 \cdot NaF$ and $WF_6 \cdot NaF$ fell into a single family of points, regardless of the order of sorption of the uranium and tungsten hexafluoride. The curve obtained for that mixture is presented in Figure 4, compared with the curves for the separate complexes and a calculated curve for the sum of the separate complexes.

The equilibrium pressure data for mixed $UF_6 \cdot NaF$ with $MoF_6 \cdot NaF$ and mixed $WF_6 \cdot NaF$ with $MoF_6 \cdot NaF$ fell on the curve for $MoF_6.NaF$ and are not shown. (The summation curves are both so close to $MoF_6 \cdot NaF$ that they could not be distinguished.)

Conclusions

The complexes $UF_6 \cdot NaF$, $WF_6 \cdot NaF$, and $MoF_6 \cdot NaF$ and the three equimolar mixtures of the complexes have been prepared by gas–solid reactions. Their successful preparation depended upon the pretreatment of the sodium fluoride.

The empirical formulas for the complexes are derived from the stepwise formation of the $MF_6 \cdot 2NaF$ and $MF_6 \cdot NaF$ compounds, chemical analyses of each product, and the specific equilibrium pressure curve for each complex. The absence of other steps or other equilibrium pressures at other ratios precludes the presence of other complexes. The temperature, pressure, and solid composition data indicate absence of solid solutions for the compounds $UF_6 \cdot NaF$, $WF_6 \cdot NaF$, and $MoF_6 \cdot NaF$.

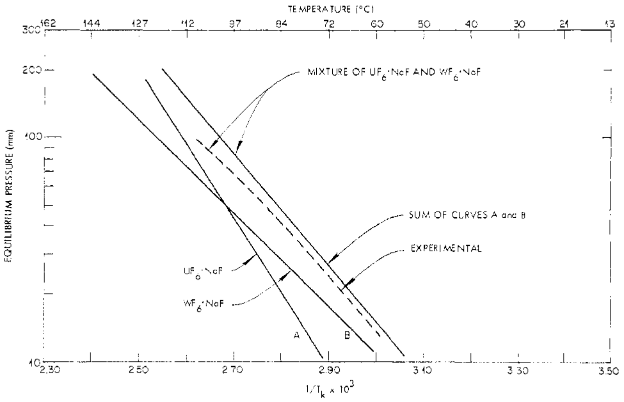

Figure 4.—Equilibrium pressures for mixed complexes; experimental and calculated values compared to equilibrium pressures of component complexes.

An indication of whether the mixed complexes are solid solutions or exist with complete absence of interaction may be inferred from the comparisons of the measured curves to curves for the individual complexes and to curves produced by plotting sums of the pressures of the individual complexes. From these data it appears that the $UF_6 \cdot NaF$–$WF_6 \cdot NaF$ mixture lies between the two states but closer to the condition of complete absence of interaction. The two mixed complexes, $UF_6 \cdot NaF$–$MoF_6 \cdot NaF$ and $WF_6 \cdot NaF$–$MoF_6 \cdot NaF$, both appear to satisfy the conditions for complete absence of interaction.

The failure of molybdenum hexafluoride to sorb well on either the $UF_6 \cdot 2NaF$ or the $WF_6 \cdot 2NaF$ appears due to the relative instability of the MoF_6 complex in each series of complexes.

The superior sorption characteristics of the uranium hexafluoride treated sodium fluoride appear to result from the retention in the solid sodium fluoride of position vacancies formerly occupied by the uranium hexafluoride.

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