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Use of High-Surface-Area Sodium Fluoride to Prepare $MF_6 \cdot 2NaF$ Complexes with Uranium, Tungsten, and Molybdenum Hexafluorides

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Successful preparation of $MF_6 \cdot 2NaF$ compounds by gas–solid reactions is shown to be dependent on the use of high-surface-area sodium fluoride and proper reaction temperatures. The reaction was fastest with UF_6 and proceeded most closely to completion, whereas with WF_6 and MoF_6 the reaction was slower and not as complete. No compound containing less MF_6 than the compound $MF_6 \cdot 2NaF$ was noted. The dissociation pressures were determined to be

UF_6 over $UF_6 \cdot 2NaF$ $\log P_{mm} = 9.25 \pm 0.02 - (4.18 \times 10^3)/T_k$
WF_6 over $WF_6 \cdot 2NaF$ $\log P_{mm} = 8.80 \pm 0.01 - (3.99 \times 10^3)/T_k$
MoF_6 over $MoF_6 \cdot 2NaF$ $\log P_{mm} = 8.27 \pm 0.07 - (2.87 \times 10^3)/T_k$

This report describes the preparation, by gas–solid reactions, of solid complexes of sodium fluoride with uranium hexafluoride, tungsten hexafluoride, and molybdenum hexafluoride (mixed with some unreacted NaF) of the formula type $MF_6 \cdot 2NaF$, and the measurement of the dissociation pressures of the metal hexafluorides over these complexes.

Recent work has firmly established the existence of $UF_6 \cdot 2NaF$, although early workers were able only to sorb UF_6 onto NaF to approximately the composition $UF_6 \cdot 3NaF$.[1–5] In 1957 Cathers and co-workers[6] reported a UF_6 content in excess of the formula $UF_6 \cdot 3NaF$. In 1961 Sheft, Hyman, Adams, and Katz[7] concluded from ^{18}F exchange studies that the compound $UF_6 \cdot 2NaF$ existed. Finally, Malm and Selig[8] in 1962 demonstrated that useful quantities of $UF_6 \cdot 2NaF$ and $UF_6 \cdot NaF$ could be prepared from reactions of uranium hexafluoride with sodium fluoride suspended in a fluorocarbon (C_7F_{16}).

Since a coordination number of 7.9 has been calculated for tungsten and molybdenum complexes of the type discussed here,[9] the failure of Cox, Sharp, and Sharpe,[10] Groves,[11] and Cathers[12] to sorb large quantities of tungsten or molybdenum hexafluoride on sodium fluoride presents an enigma. This is especially so, considering the simple preparation of $MoF_6 \cdot 2KF$, $MoF_6 \cdot 2RbF$, $MoF_6 \cdot 2CsF$, $WF_6 \cdot 2KF$, $WF_6 \cdot 2RbF$, and $WF_6 \cdot 2CsF$[10] by reactions between the gaseous fluorides and solid alkali fluorides and the preparation of $UF_6 \cdot 2NaF$ by the gas–solid reaction reported here.

Experimental

Materials.—The sodium fluoride was in the form of $^1/_8$-in. diameter cylindrical pellets prepared by Harshaw Chemical Company (lot 10). The uranium hexafluoride was from a local supply and was purified by repeated liquefaction and flashing cycles until a vapor pressure of 17 mm. was achieved at 0°. The tungsten hexafluoride was from a local supply and contained less than 0.1% of impurities. The molybdenum hexafluoride was supplied by General Chemical Co. and was purified by flashing at 0° until a vapor pressure of 167 mm. was achieved.

Gasometric Apparatus.—The principal components of the apparatus are the gas buret and the reactor. The buret has a volume of 559 cc. and contains 2.34 mmoles of gas at 110° per 100 mm. pressure. For each gas used, the delivery was cross-checked gravimetrically. The reactor was a quick-opening type of 152-cc. volume enclosed in a copper block for temperature stability; a furnace fitted over the copper block. The gas capacity of the reactor was calibrated as a function of temperature. All surfaces exposed to corrosive gases are of resistant metals, principally nickel.

Preparation of the Sodium Fluoride Complexes with Hexafluorides of Uranium, Tungsten, and Molybdenum.—For each preparation, 0.42 g. of sodium fluoride (10 mmoles) was placed on a nickel tray in the reactor. The reactor was then sealed and leak tested, and the sodium fluoride made more reactive by the following procedure: With the reactor at 25 to 50°, hydrogen fluoride was introduced until over 40 mmoles had been sorbed by the sodium fluoride; the reactor was then evacuated by pumping and heating to 250°, with further pumping to remove the hydrogen fluoride. The bulk density of this sodium fluoride fell from 1.5 to 0.5 g./cc., and the surface area increased from 1 m.^{2}/g. to as much as 7 m.^{2}/g. The surface areas were measured by the nitrogen adsorption (BET) method.

The uranium hexafluoride, tungsten hexafluoride, or molybdenum hexafluoride was transferred, as needed, into the sample flasks and buret inside the 110° box The sample in the reactor was then exposed for no longer than 24 hr. to a measured quantity of MF_6 gas selected such that the final pressure of the gas over the complex formed was equal to 110 to 120 mm.

The temperature of the reactor during the sorption was maintained near the optimum for each gas. Significantly marked variations in the adsorption characteristics were noted among the three gases, according to the temperature. The uranium hexafluoride was sorbed rapidly, with no difference found between 100 and 200° and no sharp change outside that range. The tungsten hexafluoride sorbed slightly slower than the uranium hexafluo-

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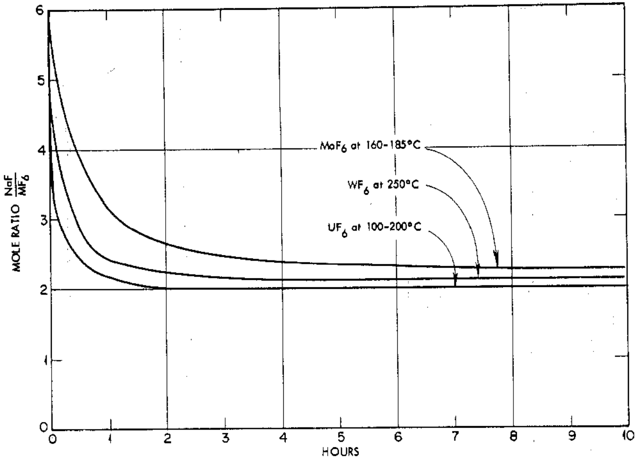

Fig. 1.—Sorption curves.

ride, with only minor rate variations between 190 and 350° (the highest temperature tried) and an abrupt reduction in rate below 190°. The molybdenum hexafluoride was sorbed much slower than either of the other hexafluorides, with the highest rate occurring between 160 and 185°. Outside this range, abrupt reductions in the rate of adsorption were found. Representative sorption curves are shown in Fig. 1, for each gas at the temperature where the rate was maximum. The uranium hexafluoride complex was yellow, while the tungsten hexafluoride and molybdenum hexafluoride complexes were white.

The resultant $MF_6:NaF$ mole ratio, measured gasometrically, and the chemical determination of the uranium, tungsten, or molybdenum in the complex formed are shown in Table I for a number of preparations.

TABLE I

GASOMETRIC AND CHEMICAL ANALYSIS DATA

	Metal hexafluoride sorbed		
	UF_6	WF_6	MoF_6
$NaF:MF_6$ mole ratio found by gasometric anal.	1.97	2.12	2.23
	2.04	2.13	2.14
	1.99	2.08	2.34
	2.02		
	2.02		
	2.02		
	Av. 2.01	Av. 2.11	Av. 2.24
Calculated wt. % of U, W, or Mo in $UF_6\cdot 2.01NaF$, $WF_6\cdot 2.11NaF$, and $MoF_6\cdot 2.24NaF$, respectively (see averages)	54.54	47.57	31.55
Found wt. % of U, W, and Mo in respective complexes	53.55	46.03	29.68
	54.03	46.57	31.98
		45.35	

A comparison of the weight percentages of uranium, tungsten, and molybdenum in the preparations shows that the values calculated from the gasometric measurements are systematically higher by about 1%. This bias is assigned to a nickel impurity introduced from the sample tray during the various operations and to water pickup during the transfer and storage of the complexes.

Results

The Dissociation Pressures of the Sodium Fluoride Complexes with Hexafluorides of Uranium, Tungsten, and Molybdenum.—In the preferred method for measuring the dissociation pressures, the complexes, prepared as described in the preceding section, were brought to a desired temperature in the reactor. The gas above the complex in the reactor was removed by pumping, taking care to remove only a small fraction of the metal hexafluoride. After closing off the reactor, the pressure of the freshly desorbed metal hexafluoride was recorded as a function of time so that the equilibrium pressure could be determined. Frequently, the gas evolved from the initial measurement was removed, and a new measurement was made on freshly evolved gas. Each succeeding pressure measurement was made with a different MF_6 : NaF ratio; no concentration dependence was evident. Another method of measuring the dissociation pressures, that of reaching the equilibrium starting from a higher pressure, was used for at least several points in each chemical system to verify that the reaction was reversible; however, the method was not preferred because attainment of steady state was generally slower and greater possibility existed for error due to the presence of impurity gases.

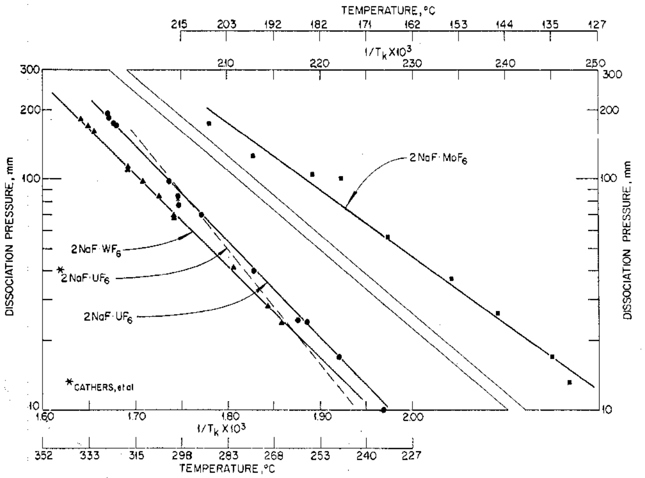

Fig. 2.—Dissociation pressure curves.

The measured dissociation pressures and the corresponding temperatures[13] are plotted in Fig. 2 in the conventional manner, log P_{mm} *vs.* $1/T_k$, along with the straight line fitted by the least-squares method. The equations for the lines are

$$\log P_{mm} = 9.25 \pm 0.02 - (4.18 \times 10^3)/T_k$$

UF_6 over $UF_6\cdot 2NaF$

$$\log P_{mm} = 8.80 \pm 0.01 - (3.99 \times 10^3)/T_k$$

WF_6 over $WF_6\cdot 2NaF$

$$\log P_{mm} = 8.27 \pm 0.07 - (2.87 \times 10^3)/T_k$$

MoF_6 over $MoF_6\cdot 2NaF$

The relatively large scatter for the points plotted for $2NaF\cdot MoF_6$ system results from the slower approach to steady state in that case.

Only for the $UF_6\cdot 2NaF$ system are published data available for comparison. Cathers, *et al.*,[6] measured

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[13] Tables of decomposition pressures as a function of temperature for $UF_6\cdot NaF$, $WF_6\cdot 2NaF$, and $MoF_6\cdot 2NaF$ have been deposited with ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C., Document No. 7713. A copy may be secured by citing the Document number and remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

by the transpiration method the dissociation pressures of a compound stated to be $UF_6 \cdot 3NaF$; the equation expressing their data

$$\log P_{mm} = 10.88 - (5.09 \times 10^3)/T_k$$

is plotted in Fig. 2 as a broken line. The large number of points from this work that fall close to the broken line indicate that the compound investigated by Cathers was also $UF_6 \cdot 2NaF$. The small but significant difference in slope between the two dissociation pressure lines for $UF_6 \cdot 2NaF$ may be due to intrinsic differences in the experimental methods used.

The enthalpy changes (kg. cal./mole of evolved gas) calculated from the lines obtained from the experimental data are −19.1 ± 0.2 for uranium hexafluoride (compared to −23.2 for Cathers' data), −18.2 ± 0.3 for tungsten hexafluoride, and −13.1 ± 0.8 for molybdenum hexafluoride.

Conclusion

The compounds $UF_6 \cdot 2NaF$, $WF_6 \cdot 2NaF$, and $MoF_6 \cdot 2NaF$ have been prepared by gas–solid reaction. These compounds are predictably stable according to coordination number calculations and the preparation of related compounds but their preparation by gas–solid reaction has thwarted previous investigators.

The successful preparation was due to the use of high-surface-area sodium fluoride made by treating ordinary sodium fluoride with hydrogen fluoride in excess of the amount required to produce $NaF \cdot 4HF$ at less than 50°, followed by rapid removal of the hydrogen fluoride by pumping, and finally by heating with pumping. Also, sorption, in some cases, was very sensitive to temperature.

For a number of preparations the data suggest that the $UF_6 \cdot 2NaF$, $WF_6 \cdot 2NaF$, and $MoF_6 \cdot 2NaF$ were mixed on the average with 0.01, 0.11, and 0.24 mole, respectively, of unreacted sodium fluoride. No intermediate compounds between NaF and $MF_6 \cdot 2NaF$ were found, although previous investigators have reported intermediate compounds such as $UF_6 \cdot 3NaF$.

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Hexachlorotungstate(V) Compounds

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The alkali metal hexachlorotungstate(V) salts, $MWCl_6$, have been synthesized, where M = Na, K, Rb, and Cs. The potassium salt has been synthesized by three independent routes: (i) reaction of WCl_6 with KI at 125°, (ii) reaction of WCl_6 with K_2WCl_6 at room temperature, and (iii) reaction of $K_2WO_4 \cdot WO_3$ with CCl_4 in a sealed tube at 400°. The salts are green and can be converted into the red M_2WCl_6 salts by heating under vacuum at 280–300°. Tetraphenylarsonium hexachlorotungstate(V) has been prepared by reaction of tetraphenylarsonium chloride with tungsten(V) chloride in chlorobenzene. Magnetic susceptibilities and visible and ultraviolet spectra are reported.

Introduction

As part of a long-range program involving weak field, octahedral d^1 complexes,[1,2] we became interested in the syntheses of salts of the WCl_6^- ion. Coincidentally with our first isolation of $KWCl_6$, an article appeared by Kennedy and Peacock[3] reporting the preparation of a series of WCl_6^{2-} compounds. Since the preparative method was similar to the one we had found successful for WCl_6^- salts, we decided to undertake an investigation of the relationship between the quadrivalent and quinquevalent hexachlorotungstate compounds.

Experimental

Starting Materials.—The metal iodides used were commercially obtained reagent grade materials. NaI and KI were dried under vacuum at 110° just before use. CsI and RbI were opened, handled, and stored in a drybox.

Tungsten(VI) chloride was prepared by the reaction of WO_3 with hexachloropropylene,[4] or, alternatively, by the reaction of WO_3 with CCl_4 in a bomb.[5,6] Some WCl_6 preparations were sublimed to check the purity of the preparation.

Tungsten(V) chloride was prepared by the reaction of red phosphorus with WCl_6.[7]

Preparation of Compounds.—*All manipulations were performed in a dry nitrogen atmosphere.*

Preparation of M^IWCl_6 Compounds.—$NaWCl_6$, $KWCl_6$, $RbWCl_6$, and $CsWCl_6$ were prepared by grinding the appropriate metal iodide with an equimolar quantity of WCl_6 until a finely divided, intimate mixture was obtained. Such a mixture was dark red in color, usually also stained with some free I_2 which

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