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APPARATUS FOR THE GASOMETRIC STUDY OF SOLID-GAS REACTIONS: SODIUM FLUORIDE WITH HYDROGEN FLUORIDE AND URANIUM HEXAFLUORIDE

Sidney Katz

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ABSTRACT

A gasometric apparatus for rapidly characterizing dissociation pressures, sorption equilibrium and kinetics, chemical states and decomposition conditions has been built and tested. The method simply involves the measurement of quantities of gases reacting with or evolving from known quantities of solid. Accuracies of better than ±1% were attained.

In testing the capabilities of the new apparatus, the dissociation pressures of hydrogen fluoride and uranium hexafluoride over their respective complexes with sodium fluoride, and the decomposition of the uranium hexafluoride complex to give elemental fluorine were verified. Additionally, a test for sorption of uranium hexafluoride on sodium fluoride was developed, the existence of the compound Na_2UF_8 was demonstrated, a more active form of sodium fluoride was made, the stability of the pentavalent uranium-sodium fluoride complex was studied, data leading to a postulated new compound $(NaF)_2(UF_6)(HF)$ was obtained, and the interaction of hydrogen fluoride and uranium hexafluoride on sodium fluoride was studied.

INTRODUCTION

Decomposition pressures, sorption equilibria and kinetics, chemical states, and decomposition conditions can be rapidly and accurately characterized in a newly constructed gasometric apparatus. The method simply involves measurement of quantities of gases reacting with or evolving from known quantities of solid.

The gasometric apparatus was tested on a series of problems relating to the separation of uranium hexafluoride from gas mixtures by adsorption on sodium fluoride. That separation is of interest because of the application in the fluoride volatility processes[1,2,3] and because of the potential applications in other operations, especially those in which small quantities of uranium hexafluoride are collected or where uranium hexafluoride is recovered from a source containing it in low concentration.[4] The reaction kinetics for the formation of the uranium hexafluoride-sodium fluoride complex as influenced by the physical form of the sodium fluoride[3,5,6] and by the presence of hydrogen fluoride in the gas mixture have been studied.[7] Dissociation pressures of hydrogen fluoride[8,9,10] and uranium hexafluoride[3] over the corresponding sodium fluoride complexes and secondary reactions during adsorption of uranium hexafluoride on sodium fluoride[7] have also been measured. While the compound formed between uranium hexafluoride and sodium fluoride had been studied,[3,7,11] some uncertainty existed as to its composition.

This report provides a description of the gasometric apparatus, materials and operating procedures used, and status of studies to determine the capability of the system. The studies include:

1. A test for the sorption of uranium hexafluoride on sodium fluoride,
2. The preparation of a more active form of sodium fluoride,
3. The preparation of the compound Na_2UF_8,
4. The decomposition of the compound Na_2UF_8 to a pentavalent uranium complex of sodium fluoride and elemental fluorine,
5. The stability of the pentavalent uranium complex of sodium fluoride,
6. The dissociation pressures of hydrogen fluoride and uranium hexafluoride over their complexes with sodium fluoride,
7. The adsorption of hydrogen fluoride on the uranium hexafluoride-sodium fluoride complex, and
8. The adsorption of uranium hexafluoride on the hydrogen fluoride-sodium fluoride complex.

APPARATUS

The principal components of the apparatus are presented in Fig. 1. Inside the insulated box (at 110°C to reduce sorption, polymerization and condensation of gases) are the gas supplies, the pressure transmitters, and the gas buret. Outside the box are the bulk gas supplies, the vacuum and disposal system, and the reactor. Those

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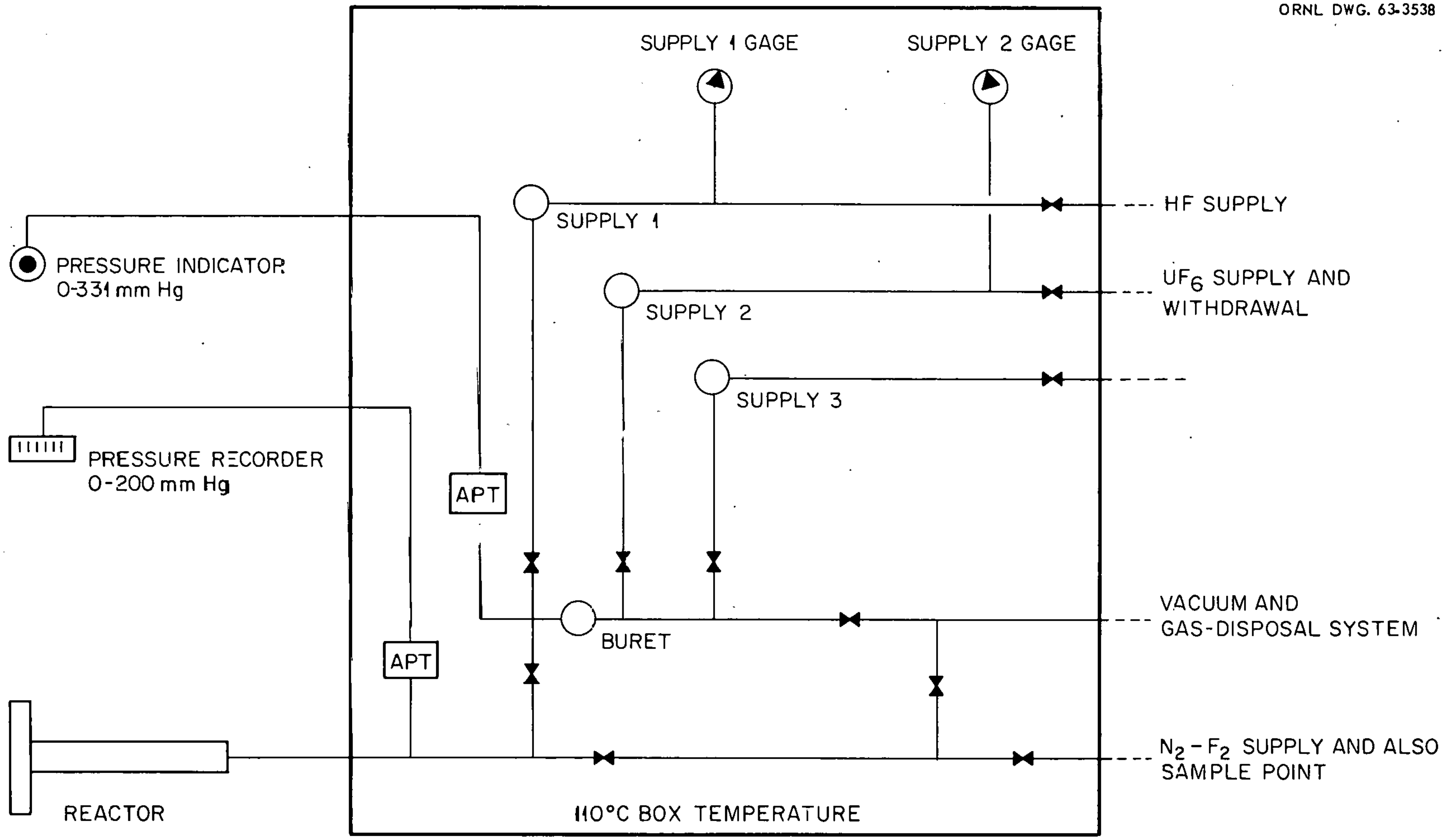

Fig. 1. Gasometric apparatus for characterizing gas-solid reactions.

components exposed to corrosive gases are of resistant materials, principally nickel. Valves are Hoke model 413.

Reactor. — The reactor is a 6-in.-long tube 1-3/8 in. in internal diameter, with a 3-in.-diam 8-holed flange. The sealing surface on the flange has four finely machined concentric lands against which a 0.005-in.-thick nickel sheet is pressed by a backing plate. Including the capillary tubing, valves and bellows of the pressure transmitter, the reactor contains 152 cc. It is mounted horizontally within a 3-in.-diam copper block so that a furnace can be conveniently placed around the block. A control thermocouple is within a horizontal hole in the copper block, and a measurement thermocouple is centrally located in a small gas space between the back of the reactor and the copper block. Temperature adjustment and measurements within 0.5°C are readily made. The temperature calibration was validated at 100°C (boiling water was used) and at 231.9°C (the melting point of tin).

Buret. — The buret consists of 40.2 cc of volume in tubing, valves and bellows of the pressure transmitter. This volume may be increased by connecting with the gas supply flasks.

Gas Supplies. — Three gas supply flasks bring gases to the temperature of the heated box. Supplies 1 and 2 have bourdon gages to aid in adjusting supply pressures.

Pressure Transmitters. — Taylor absolute pressure transmitters in the ranges 0 to 200 and 0 to 331 mm Hg pressure are used in the reactor and buret respectively. Periodically the calibrations were checked against a mercury manometer.

Vacuum and Gas Disposal System. — A mechanical pump supplies vacuum through a trap composed of soda-lime and alumina (1:1).

Volume Calibrations. — Three methods were used to calibrate and cross check volume calibrations: (1) liquid displacement, (2) gas displacement from a previously calibrated volume, and (3) measurement of gas evolved during a known decomposition reaction. Gas supply 3 was first determined to contain 243.1 cc (water displacement). Gas displacement was used to determine volumes of the buret, supply 3, and the reactor to be 40.2, 276.1, and 152 cc, respectively. The total of 559 cc for the buret plus supplies 2 and 3 was verified when the same value was obtained from measurement of hydrogen fluoride evolved by decomposition of the sodium bifluoride complex. At 110°C, the buret, supply 2, and supply 3 contained 0.56, 3.83, and 3.37 millimoles of gas, respectively, when filled to 100 units on the buret-pressure-measurement system (100 units equals 331 mm Hg pressure).

MATERIALS

Sodium Fluoride. — Harshaw (lot 10) 1/8-in.-diam cylindrical pellets each weighing 0.037 g were used.

Hydrogen Fluoride. — Mathieson Company hydrogen fluoride was flashed off to remove inerts.

Uranium Hexafluoride. — Isotopically depleted uranium hexafluoride was further purified by repeated liquefactions and flashing cycles until a vapor pressure of 17 mm Hg pressure was achieved at 0°C.

PROCEDURES

Stabilization. — The system at 110°C was treated with 200 mm Hg pressure of fluorine for several hours initially and after each opening for maintenance.

Solid Sample Introduction. — The weighed sample, normally spread out on a thin nickel tray, was placed on the reactor bottom. The reactor was then sealed and leak tested by evacuation and pressure monitoring.

Gas Sample Transfers. — Gases of interest were transferred from the larger external supplies into the sample flasks inside the 110°C box as needed. The sample flasks were used to fill the buret.

Adsorption Tests. — With the solid sample at the desired temperature in the evacuated reactor, a measured quantity of gas was rapidly transferred from the buret to the reactor. The reactor pressure was recorded as a function of time.

Desorption Tests. — With the sample confined in the reactor at the desired temperature, evolved gas was measured by transferring the gas into the buret (evacuated or filled to the same pressure with the gas being desorbed). Increments of gas were transferred from the buret to the disposal system while maintaining the desorption pressure within desired limits.

Dissociation Pressure Measurements. — The solid sample in the evacuated reactor was brought to constant temperature for the pressure measurement. Frequently, the gas evolved from the measurement was removed, and a new measurement was made on freshly evolved gas.

STATUS OF STUDIES MADE WITH THE APPARATUS

A Test for Sorption of Uranium Hexafluoride on Sodium Fluoride. — The test was carried out as described under "Adsorption Tests" above, using 0.42 g of sodium fluoride (10 millimoles) and 100 on the buret pressure scale for uranium hexafluoride, with gas supplies 2 and 3 connected to the buret (7.75 millimoles equals 100 units). Application of the test to sodium fluoride pellets and "activated" sodium fluoride are presented in the following section. The test permits examination of various forms of sodium fluoride and different adsorption conditions.

A More Active Form of Sodium Fluoride. — Sodium fluoride pellets (as received) adsorbed 0.160 moles UF_6 per mole NaF on the first adsorption, followed by a drastic reduction to 0.042 on the second adsorption and a gradual increase in succeeding adsorptions as demonstrated in Fig. 2a. Conditions were as follows: pretreatment with fluorine for 12 hr at 150°C, adsorption at 135 to 145°C, and maintenance at 320°C for 1 hr prior to desorption.

Active sodium fluoride, prepared by treatment with hydrogen fluoride so as to exceed the 4:1 HF/NaF mole ratio followed by removal of the HF, adsorbed 0.5 moles UF_6 per mole NaF on the first adsorption. A gradual reduction in adsorptive capacity was noted in succeeding adsorptions, as presented in Fig. 2b. The conditions were similar to those used with the pellets except that no prior fluorine treatment was used and the adsorptions were at 150 to 170°C.

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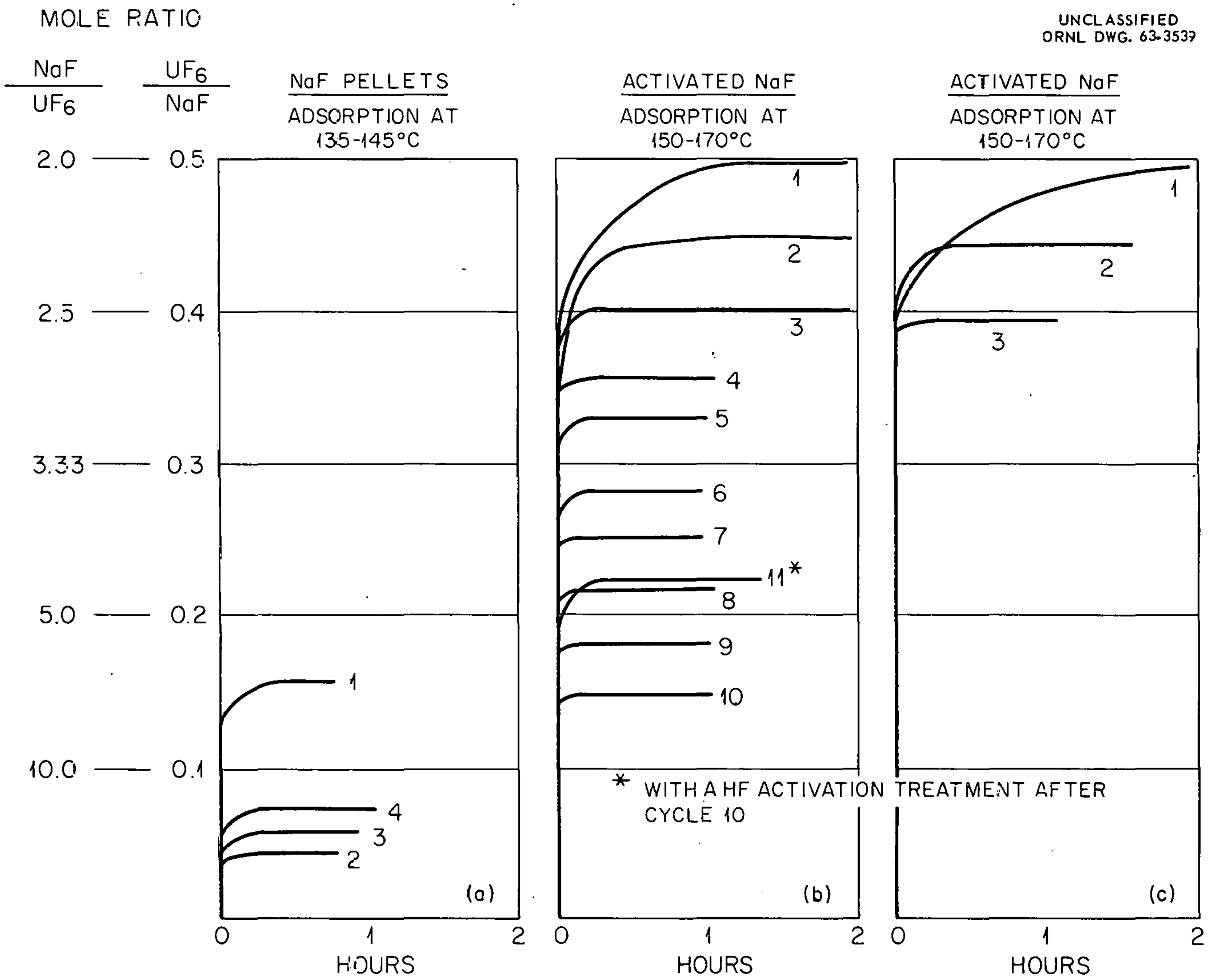

Fig. 2. Adsorption tests of uranium hexafluoride on sodium fluoride.

Repeating the adsorptions on the active sodium fluoride in the presence of 100 mm Hg pressure of fluorine resulted in no change, as shown in Fig. 2c. The residual sodium fluoride contained only 0.28% uranium. Those data indicate that change in adsorption capacity is related to physical form rather than due to accumulation of reduced uranium; the opposite conclusion may be drawn from the fact that a second hydrogen fluoride activation treatment, after the 10th cycle of the series (presented in Fig. 2b), produced only small improvement in adsorption capacity.

The adsorption "curve" and capacity were unchanged for the active sodium fluoride for the temperature range 100 to 210°C.

The active sodium fluoride preparations had densities of about 0.5 g/cc and surface areas of about 7 m^2/g, compared with 1.5 and 1 to 2 for the same properties for pellets.

A Preparation of the Compound, Na_2UF_8. — Repeated adsorptions of uranium hexafluoride on active sodium fluoride, such as those in Fig. 2b, resulted in sodium-fluoride-to-uranium-hexafluoride mole ratios of 1.97, 2.04, 1.99, 2.02, 2.02 and 2.02. In all cases, the rate of adsorption became very slow as the ratio approached 2.00. The vapor pressure of uranium hexafluoride over the complex was measured to be 17 mm at 249°C and 180 mm at 320°C, in good agreement with the dissociation pressure of the previously accepted compound Na_3UF_9. The measurements were more difficult to make than those having a higher NaF/UF_6 mole ratio, because of the apparent greater evolution of fluorine. The increase in weight upon synthesis and chemical analysis verified the formation of the compound Na_2UF_8:

Preparation	A	B	C
Starting NaF, g	0.411	0.412	0.432
Solid recovered, g	1.696	1.516	1.698
Additional uranium recovered, g	0.147	0.269	0.158
Theoretical yield, g	2.135	2.140	2.250
Actual yield (plus some lost as dust), g	1.970	2.016	1.993
Uranium in solid, % (theoretical equals 54.60)	53.55	54.03	53.60
Sodium in solid, % (theoretical equals 10.55)			11.76

Because the compound approached the mole ratio 2 from the side of excess of sodium fluoride, the sodium concentration should be slightly high and the uranium concentration slightly low.

The Decomposition of the Compound Na_2UF_8 to a Pentavalent Uranium Complex of Sodium Fluoride and Elemental Fluorine. — A white pentavalent uranium compound was prepared by reaction of 0.422 g of sodium fluoride at 393°C with excess uranium hexafluoride for about 1/2 hr; a weight increase of 0.651 g resulted. The residue contained 24.78% quadrivalent uranium and 50.15% total uranium by chemical analysis. (Pentavalent uranium compounds when analyzed similarly provide a ratio of 2:1 for total to quadrivalent uranium.) From these data, about 2 millimoles of uranium pentafluoride were deposited on 10 millimoles of sodium fluoride.

In a second test, Na_2UF_8 prepared by adsorption of uranium hexafluoride on 0.407 g of active sodium fluoride, was heated to 395°C for 1 hr. The evolved gas was passed through a sodium fluoride trap to collect uranium hexafluoride and then through a solid potassium iodide trap to collect elemental fluorine by converting the potassium iodide to potassium fluoride and liberating iodine, which was measured. The potassium iodide trap collected 0.009 g of uranium and 0.076 g of fluorine.

Stability of the Pentavalent Uranium-Sodium Fluoride Complex. — In addition to the preparations described above, a 2:1 ratio of total to quadrivalent uranium was found in the other two cases where residues were analyzed after a series of adsorption-desorption cycles. Furthermore, the pentavalent complex discussed in the second test in the section above did not evolve a detectable quantity of gas when heated to 550°C for about 1/2 hr.

The Dissociation Pressures of Uranium Hexafluoride and Hydrogen Fluoride Over Their Complexes with Sodium Fluoride. — The dissociation pressures were measured as described in "Dissociation Pressure Measurements" in the "Procedures" section. The data for the temperature ranges of 218 to 325.5°C and 153 to 229°C, respectively, for the uranium hexafluoride and hydrogen fluoride complexes are presented in Tables 1 and 2. Both sets of data are in general agreement with the previous data of Davis[9] and Fischer[10] for the hydrogen fluoride, and with the data of Cathers, Bennett, and Jolley[3] for the uranium hexafluoride complex.

Table 1. Dissociation Pressures for NaF·HF

Order of Measurement	Temp. (°C)	Pressure (mm Hg)
1	98	0
2	153	15.5
3	186	55.5
4	203	116
5	208	164
6	229	308

Table 2. Dissociation Pressures for $(NaF)_2 \cdot UF_6$

Order of Measurement	Temp. (°C)	Pressure (mm Hg)
1	218	6
14	235.5	10
2	247	17
12	257	24
13	260	24.5
3	274	40
11	291	70
5	299	84
6	299	84
4	303	97
10	322.5	173
7	323.5	177
9	325	188
8	325.5	194

The slope of the uranium hexafluoride line [logarithm of pressure plotted vs 1/T(°K)] varies slightly from that determined by Cathers, Bennett, and Jolley, giving a higher extrapolated value of 376°C rather than their 363°C for the temperature at which 1 atm of pressure would be reached. This difference will be investigated further when modification of the gasometric apparatus permits more accurate measurements at higher pressures.

The Adsorption of Hydrogen Fluoride on the Uranium Hexafluoride-Sodium Fluoride Complex. — A previously prepared uranium hexafluoride-sodium fluoride complex (4.85 millimoles of Na_2UF_8) was exposed to 200 mm Hg pressure of hydrogen fluoride at 200°C. The pressure was monitored as the temperature was reduced; at 75°C adsorption became evident. The system temperature was taken to 62°C and adsorption continued until the adsorption rate became very slow (3 hr), at which time 4.93 millimoles of hydrogen fluoride had been adsorbed to make the complex, $(NaF)_2(UF_6)(HF)$.

The dissociation pressures measured from 59 to 105°C are given in Table 3. Since the vapor pressure curve appears to be a straight line and the points were reproducible after removal of gas evolved in earlier measurements and regardless of order of being made, a definite compound had been present, and a gas of constant composition has been evolved. At 125°C 2.87 moles of gas had been evolved. The remaining residue when heated to 202.5°C provided a dissociation pressure of 105 mm Hg, very close to the pressure of hydrogen fluoride over the sodium fluoride complex; 2.34 millimoles of gas, presumably hydrogen fluoride was then removed at about 200°C. The final residue contained 49.29% uranium (chemical analysis) or about 5% less than would be expected if uranium hexafluoride had not been displaced. From the material balance, the gas evolved from the $(NaF)_2(UF_6)(HF)$ complex was 16% uranium hexafluoride and 84% hydrogen fluoride.

If, as indicated by the dissociation pressure measurement at 202.5°C, the hydrogen fluoride and uranium hexafluoride complexes of sodium fluoride are mixtures at that temperature, hydrogen fluoride can be separated from mixed beds at about 200°C.

Table 3. Dissociation Pressures for $(NaF)_2 \cdot UF_6 \cdot HF$

Order of Measurement	Temp. (°C)	Pressure (mm Hg)
1	59	10
7	70.5	23
2	84	67
6	85	59
3	96	120
5	100	145.5
4	105	197

The Adsorption of Uranium Hexafluoride on the Hydrogen Fluoride-Sodium Fluoride Complex. — No adsorption of uranium hexafluoride upon the sodium bifluoride complex was noted down to 45°C.

DISCUSSION AND CONCLUSIONS

The gasometric apparatus operated satisfactorily. Precision of gas transfers were better than ±1.0%. Accuracy in synthesizing compounds was within 1.0%. The manipulations are simply and rapidly performed. Mechanical problems in operating the system were minor. Pressure and temperature calibrations remained stable.

The need for modifications became apparent. The most important are: (1) increase the sensitivity and range of pressure measurements, and (2) provide a gas-sampling point.

Where previous data were available, the data obtained with the gasometric apparatus agreed well. In a number of areas under study, new information and a better understanding of the chemistry involved has already resulted.

ACKNOWLEDGEMENT

Charles Schilling is responsible for a number of mechanical refinements to the apparatus; I am particularly grateful for the seal design. Most of the construction was done by Tom Crabtree.

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