Preparation of yttrium fluoride using fluorine

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Calculations made using the best data available at this time show the reaction of yttrium oxide with fluorine gas is a highly exothermic reaction which would be expected to proceed spontaneously to almost complete conversion. A theory is presented which attempts to explain why this did not occur under the conditions imposed.

It was demonstrated that fluorine gas supplied in pressure cylinders can be safely handled in a laboratory hood under the conditions cited above if proper precautions are taken.

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PREPARATION OF YTTRIUM FLUORIDE USING FLUORINE

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June 1959

Ames Laboratory
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PREPARATION OF YTTRIUM FLUORIDE USING FLUORINE*

by
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Summary- This report deals with the preparation of a low oxygen content yttrium fluoride using commercial fluorine gas. It was shown that the purity of yttrium fluoride prepared using hydrogen fluoride gas could be improved by treating it with fluorine (1) at a temperature of 600°C under pressures in the range 20-25 psig or, to a lesser degree, (2) at 25°C and 1 atmosphere pressure.

Preparation of yttrium fluoride by direct fluorination of yttrium oxide was found to be a spontaneous process which ceases short of equilibrium under the conditions studied. Fluorination of yttrium chloride resulted in a more complete conversion than that obtained with the oxide, but the degree of conversion was not high enough to be of interest.

Calculations made using the best data available at this time show the reaction of yttrium oxide with fluorine gas is a highly exothermic reaction which would be expected to proceed spontaneously to almost complete conversion. A theory is presented which attempts to explain why this did not occur under the conditions imposed.

* This report is based on a Master of Science thesis by R. L. Tischer, submitted to Iowa State University, June 1959. This work was done under contract with the U. S. Atomic Energy Commission.
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It was demonstrated that fluorine gas supplied in pressure cylinders can be safely handled in a laboratory hood under the conditions cited above if proper precautions are taken.

INTRODUCTION

The method currently employed for producing massive yttrium metal at the Ames Laboratory is the metallothermic reduction of yttrium fluoride. The production of a minimum oxygen content fluoride has been the subject of investigation in an effort to reduce the amount of oxygen appearing in the product metal. Previous work\(^{(1, 2)}\) focused on the use of hydrofluoric acid as the fluorinating agent. The present effort was directed to an investigation into the feasibility of producing yttrium fluoride using elemental fluorine as the fluorinating agent. Its use was investigated to determine if the greater reactivity of fluorine could be used to produce an yttrium fluoride superior in quality to that produced by other methods.

Direct fluorination of yttrium salts is a reaction that is difficult to control due to the large amounts of heat liberated during the course of the reaction. The handling of fluorine is considered to be more difficult than the handling of anhydrous

\(^{(1)}\) O. N. Carlson, F. A. Schmidt and F. H. Spedding, Preparation of Yttrium Metal by Reduction of Yttrium Trifluoride with Calcium, ISC-744 (1956).

hydrogen fluoride gas because of its greater reactivity, higher heats of reaction, and the fact that it is supplied as a pressurized gas while anhydrous hydrogen fluoride is supplied as a liquid.

Corrosion encountered using fluorine constitutes a major problem, and this problem magnifies itself greatly as higher temperatures are used. Because of this corrosion problem and the physical hazards to both equipment and personnel associated with exposure to jets of the high pressure gas, the use of fluorine under pressure is generally avoided if possible. The use of remote control is mandatory from a safety standpoint when handling fluorine under pressure. Since fluorine reacts spontaneously with most oils and organic materials, precautions of an extraordinary nature must be taken to insure cleanliness of equipment.

At the time this work was undertaken there were no data available to permit the calculation of the heat or free energy of reaction. Recently, however, estimates of the information previously lacking have become available and the calculated values are presented.

EQUIPMENT

A schematic of the system employed in this investigation is shown in Fig. 1. It may be conveniently broken down into three components: (1) a high pressure section in which the fluorine from the cylinder is throttled from a cylinder pressure of as high as 400 psig to approximately 50 psig, (2) a low pressure reaction section, and (3) a waste gas disposal section. Provision was also made for the introduction of an inert gas into the high pressure section for any one of
three functions, i.e., for pressure preloading the high pressure section, for flushing the apparatus, and for diluting the fluorine gas stream.

The high pressure section is shown under line A-A in Fig. 1. The entire section, with the exception of the pressure gauge PGH, was contained in a protective shell made of 1/8 inch steel plate. This steel shell was bolted to a plywood panel which formed the wall between the walk-in hood containing the apparatus and the adjacent hood which served as the control area. The control area is shown in Fig. 2a. The cylinder valve, designated V-1, was manipulated by means of a socket wrench fitted down through a hole in the top of the shell over the valve stem. A racheted extension handle, operated through a slot in the plywood panel, served to accomplish the change in direction necessary to operate this valve from the control area. The slot and the handle can be seen in Fig. 2a.

A panel, shown in Fig. 2b, was fitted into place and secured just inside and across the open side of the steel shell near the top. To the cylinder side of this panel were mounted valves V-3, V-4, V-5, and V-6. These valves were provided with extension handles enabling remote operation from the control area in the adjacent hood, as can be seen in Fig. 2a. All valves used in contact with the high pressure fluorine were Hoke M-440 bellows seal valves.

An adapter for the fluorine cylinder was fabricated from brass rod. It consisted of an outer nut and an inner piece (rod), fitting into the outlet pipe of the cylinder valve on one end, and on the other end into a shoulder on the inside of the nut. This piece was bored down the middle to the same size as the hole
Fig. 1. Schematic of unit for fluorinating yttrium materials.
Fig. 2. Photographs of apparatus used for fluorination studies.

a. Control area located in walk-in hood adjacent to hood actually containing the fluorination apparatus.

b. View showing panel-mountings. The controls for the high pressure section are mounted on the panel inside the steel shell. The indicating instruments and controls for the low pressure section are mounted on the panel affixed to the top of the steel shell. The shielded light on the left was used to illuminate the indicating instruments.

c. Operators view of indicating instruments looking through the Plexiglas window. The location of the window can be seen in Fig. 2a.

d. View of apparatus as it would appear during the course of an experiment.

e. Disposal section used to consume excess fluorine and conduct combustion products to duct of hood.
in the cylinder valve outlet pipe. The two bearing surfaces were gasketed with Teflon gaskets. Tightening the nut thus provided a good gas-tight connection. Piping in the high pressure section consisted of 1/4 inch soft copper tubing and the fittings were of brass. Soft copper tubing connections were flare-fitted and sealed by brazing. These connections were not observed to leak at any time.

A collar of steel plate was fitted about the top of the cylinder under the valves and other piping, and a front cover of steel plate was suspended by means of leaf hinges from the top of the steel shell on the open side to a point below the collar. In this way provision was made to safeguard against the spread of a fire by jets of high pressure fluorine and molten reaction products should a leak develop in the high pressure section. A piece of transite placed against the open side of the steel shell served as an insulator to protect the cylinder from heat generated by the furnace and as an added protective measure in enclosing the high pressure section. By utilizing hinge suspension for the front cover, this piece could be conveniently moved up and out of the way when changing cylinders. These features can be seen in Fig. 2b.

One of the purposes of the low pressure section was to obtain accurate metering of the gas flow rate through the system. Metering was accomplished using a Brooks rotameter, designated R-F in Fig. 1. Shielded to insure safety, the rotameter had steel end-fittings, a pyrex glass metering tube, a spherical aluminum float and a detachable scale. The pressure gauge PGL indicated the pressure under which the rotameter was operating. Both pressure gauges, PGH and PGL, were Duragauges manufactured by the Ashcroft Division of Manning,
Maxwell, and Moore, and employed silver soldered bronze bourdon tubes as the sensing elements.

The two pressure gauges, the rotameter R-F, and valves V-2 and V-7 were mounted on a panel affixed to the top of the steel shell, as shown in Fig. 2b. Valve V-7 was a Hoke M-440 bellows seal valve while valve V-2 was a needle valve constructed of type 316 stainless steel having a stainless seat and Teflon packing. These valves were also equipped with extension handles which permitted their operation from the control area. The pressure gauges and the rotameter R-F were visible to the operator in the control area through a Plexiglas window in the plywood panel. Figure 2c shows the operator's view looking through this window.

The original reaction section was of aluminum construction since this material has very good resistance to fluorine corrosion. Copper was used in later experiments at higher pressures and temperatures. Essentially the reaction section consisted of a tube in which a boat containing the sample to be fluorinated was placed. A Teflon-gasketed flange connection was used to break the system, permitting the insertion or removal of the sample-containing boat. To insure a good seal at the flange, the tubes were extended completely through the flanges and were made to protrude 1/32-1/16 inch so that when the flanges were drawn up the metal would bite into the gasket. The location of the flange in relation to the reaction chamber can be seen in Fig. 2d. It should be pointed out here that the line containing the pressure gauge and valve seen in the upper left hand corner of Fig. 2d were added subsequent to this work for the purpose of carrying out high-pressure hydrofluorination experiments and thus are not shown on the schematic in Fig. 1.
Beyond the flange a tee was used to give access for the thermocouple well and insure its being centered, the branch of the tee being used to conduct the effluent gases to disposal. Valve V-8 was a needle valve, of the same construction as valve V-2, used either to provide back-pressure when it was desired to run the reaction under pressure or to close the system to the atmosphere when not in use. The entire reaction chamber was supported in a hinged-type resistance furnace capable of supplying external heat when desired.

The effluent gases from the reaction section were burned in a Meker burner with natural gas and air. The effluent gases were conducted into the burner through a port drilled 1/2 inch down from the top of the chimney of the burner. The combustion products were immediately drawn into a hard copper tube located directly above the burner and conducted to the ductwork of the hood. Use of this tube prevented the gases from spreading throughout the hood. A pilot light was provided to insure against the flame going out during operation. These details can be seen in Fig. 2e.

The draft on the hood was high enough that the maximum concentration of fluoride ion leaving the hood, expressed as ppm HF, was below the tolerance level of 3 ppm. The exit end of the tube was so located in the duct that the current of air passing its mouth created a vacuum at this point, and hence a draft in the tube itself.

The apparatus described was the result of many revisions from the one originally planned. The piping in this original apparatus was to be type 309 stainless steel. Difficulties in procuring fittings led to the use of some type 347 and type 304 stainless steels. Numerous attempts to weld these materials proved
to be futile due to leaks which appeared in the welds. While attempting to seal one leak, others would develop. Also originally included were a gas mixing chamber and a preheater. The preheater was abandoned when work with a similar hydrogen fluoride system showed it was not necessary. The mixing chamber did not appear to have any great merit in the new design and was eliminated.

The use of only one valve to throttle the fluorine to 50 psig made control difficult but not impossible. Two valves were included in the original design for this task but when the design was modified the second valve was required elsewhere. Two valves here would give smoother operation and easier control. The Hoke M-440 valves gave trouble-free operation during the entire time the system was in operation, but the valve V-8 of stainless steel suffered from pitting and corrosion of the needle and seat which made control of the back pressure in the later experiments difficult. It finally seized tightly enough to cause the valve stem to shear off during the final experiment.

**TOPPING OF YTTRIUM FLUORIDE**

Experiments were performed to determine if the purity of yttrium fluoride produced by other methods could be improved by treatment with fluorine. Such a treatment was called "topping".

Three different "grades" of yttrium fluoride were used. "Grade 1" was produced by the metallurgy group of the Ames Laboratory by hydrofluorination of yttrium oxide using anhydrous fluoride gas at 800°C for 8 hours. "Grade 2" was produced by the chemical engineering group of the Ames Laboratory by reacting yttrium oxide with ammonium bifluoride. This material was more fluffy and less dense than the other grades. "Grade 3" yttrium fluoride was from another batch
prepared by the metallurgy group and was thought to represent some of the best yttrium fluoride, in terms of purity with respect to oxygen, available at the time in this Laboratory.

The fluorine gas flow rate used in all experiments was 1.125 liters per minute measured at 24°C and atmospheric pressure. The internal cross-sectional area of the reaction tube was 0.0136 square feet, which gave a linear velocity of the fluorine over the sample of 2.92 feet per minute at the above-mentioned conditions.

The first series of eight experiments was conducted at 300°C using grades 1 and 2 material. A 3/8 inch sample bed depth and conversion times of one and three hours were used. The temperature was first raised to 300°C with the sample under nitrogen, the fluorination carried out for the specified length of time, and the sample then cooled under nitrogen flow.

The samples were analyzed for oxygen using the spectrographic technique. By this method yttrium fluoride samples are arced in an argon atmosphere and a ratio of the intensity of the oxygen line to that of an argon reference line is determined. This ratio can then be used as an indication of the relative amounts of oxygen in different samples. Throughout this report the ratios reported are of the intensity of the oxygen line at 7771 Å to the intensity of the argon line at 7891 Å.

Seven sets of analyses were averaged to give an intensity ratio of 0.76 for grade 1 material, and 0.49 for grade 2. No reduction in these ratios was obtained during the first series of runs regardless of the conversion time employed.
The second series of experiments was conducted at room temperature. Two
one-hour experiments using grade 1 fluoride were designed to test the effect of
the lower temperature and two other one-hour experiments using grade 3 material
were designed to test the effect of particle size. In the particle size experiments,
the bed was kept as thin as possible to minimize any diffusion effects. The bed for
these cases was only a few particles deep at its deepest points.

A control sample of the starting material was submitted for analysis with the
treated samples in the particle size experiments. The control sample was selected
directly from the material to be treated and all subsequent handling was carried
out as uniformly as possible. The sample was taken after the material had been
screened but before it had been treated. Table I shows the results of the particle
size experiments. The letter C designates the control.

Table I

Data for Experiments on Topping of Yttrium Fluoride (Grade 3) of
widely Varying Particle Size. (One hour, 25°C, 1 atm)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth of sample</th>
<th>Particle size</th>
<th>Intensity ratio</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-C</td>
<td>-</td>
<td>-325 mesh&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.50, 0.45, 0.37</td>
<td>0.44</td>
</tr>
<tr>
<td>6</td>
<td>UT&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-325 mesh</td>
<td>0.56, 0.47, 0.45</td>
<td>0.49</td>
</tr>
<tr>
<td>7-C</td>
<td>-</td>
<td>+ 60 mesh&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.42, 0.43, 0.44</td>
<td>0.43</td>
</tr>
<tr>
<td>7</td>
<td>UT</td>
<td>+ 60 mesh</td>
<td>0.46, 0.50, 0.48</td>
<td>0.48</td>
</tr>
</tbody>
</table>

<sup>a</sup>Particles passed through 325 mesh Tyler screen.

<sup>b</sup>Depth of sample only a few particles deep at deepest point.

<sup>c</sup>Particles retained on 60 mesh Tyler screen.
The values for the untreated grade 3 material reported above as controls do not represent the total number of analyses made on this material. In all, 18 separate analyses were carried out on this material. The spectrographic group reported a standard deviation of 0.07 intensity units for analyses in this range. This figure was arrived at by analyzing a corresponding sample of the material 270 times. The average value for the grade 3 material over the 18 separate analyses was found to be 0.40. Of the 18 values obtained, only two varied by more than 0.07 intensity units from this average value.

Comparing the intensity ratios for samples 6 and 7 before and after topping, the data seem to suggest that the oxygen content had increased. The interesting fact was that the increase seemed to be independent of particle size. On the basis of these results and some results obtained with the direct fluorination of the oxide, which will be presented later, it was concluded that the apparent particle size of the solid reactant material did not greatly influence the rate or degree of reaction. This is also true of the fluoride produced from yttrium oxide by hydrofluorination if the intensity ratios reported for samples 6-C and 7-C in Table I are considered to be representative.

In Table II the results of the runs made to determine the effect of temperature are reported. Runs 5-F and 6-F from the first series at 300°C are included to demonstrate the absence of any improvement in conversion over the control, which represents the starting material for all runs in Table II. At 25°C a significant reduction in intensity ratio and hence oxygen in the fluoride is apparent.
Table II

Analyses of Yttrium Fluoride Topped with Fluorine Gas at One Atm. and Different Temperatures.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Grade</th>
<th>Conversion time, hr.</th>
<th>Temperature; °C</th>
<th>Intensity ratio</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1</td>
<td></td>
<td>300</td>
<td>0.70, 0.76, 1.19, 0.65, 0.95, 0.99</td>
<td>0.76</td>
</tr>
<tr>
<td>5-F</td>
<td>1</td>
<td>1</td>
<td>300</td>
<td>0.84, 0.51, 0.93, 0.66, 0.40, 1.09</td>
<td>0.74</td>
</tr>
<tr>
<td>6-F</td>
<td>1</td>
<td>1</td>
<td>25</td>
<td>0.43, 0.40, 0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>1</td>
<td>25</td>
<td>0.41, 0.46, 0.39</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Next to be studied was the effect of pressure on the reaction. It was not known whether the oxygen was present in the yttrium fluoride as unreacted yttrium oxide, yttrium oxyfluoride, or a mixture of the two. Nonetheless, a look at the equations for the reactions,

\[ \text{Y}_2\text{O}_3 + 3 \text{F}_2 = 2 \text{YF}_3 + 1.5 \text{O}_2 + \text{Heat}, \]

and

\[ \text{YO}_2 + \text{F}_2 = \text{YF}_3 + 0.5 \text{O}_2 + \text{Heat}, \]

reveals that, according to the LeChatelier-Braun Principle, an increase in pressure will favor the production of yttrium fluoride regardless of how the oxygen is present in the fluoride. A bed depth of 0.125 inches was used for these experiments.
The first topping experiment carried out in a pressurized reaction chamber was conducted at 25°C. The succeeding experiments were conducted at temperatures which would test the ability of the apparatus to withstand higher temperatures as well as give some information on the effects of temperature on the conversion obtained. Accordingly, the second experiment was conducted at 600°C. Upon completion of this experiment it was found that the aluminum boat used was in a very deteriorated condition, having sagged noticeably in the middle section. The metal in this portion of the boat had become very flaky. The condition of the metal was such that in removing the boat a piece of the metal fell out of the bottom. However, the sample appeared very white and none of the sample material had been lost through the hole. This was because the material had become somewhat packed. It was concluded that heat being supplied by the reaction had been sufficient to momentarily raise the temperature of the aluminum to its melting point (660°C) and that the metal had then started to flow.

The results of the experiment at 600°C were encouraging enough that it was decided to try an experiment at a still higher temperature. A copper boat was fabricated to contain the sample. Up to this time copper in the reaction zone appeared to have suffered very little corrosion. The temperature rose steadily to 716°C over a period of two hours. At this point failure of the copper reaction chamber occurred, and the run was necessarily terminated short of the 3 hours planned. This failure of the reaction chamber was unfortunate from the standpoint that it occurred before the reaction had run its allotted time, but it was beneficial in that it demonstrated that failure under high temperature and pressure could be handled with dispatch and without hazard. The results of the three experiments run under pressure are tabulated in Table III.
Table III
Analyses of Yttrium Fluoride (Grade 3) Topped with Fluorine Gas at 20 PSIG.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Conversion time (hr)</th>
<th>Final conversion temperature (°C)</th>
<th>Intensity ratio</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td></td>
<td>0.40</td>
</tr>
<tr>
<td>08</td>
<td>3</td>
<td>25</td>
<td>0.43, 0.42, 0.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.43, 0.43, 0.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.36, 0.35, 0.33</td>
<td>0.39</td>
</tr>
<tr>
<td>09</td>
<td>3</td>
<td>600</td>
<td>0.29, 0.31, 0.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.35, 0.35, 0.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.36, 0.31, 0.32</td>
<td>0.33</td>
</tr>
<tr>
<td>002</td>
<td>2</td>
<td>700</td>
<td>0.29, 0.36, 0.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.35</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Visual examination of the copper reaction chamber showed the failure had occurred locally, four holes having developed close to one another. The copper was examined metallographically but the reason for the failure could not be determined. The tube was measured with a micrometer and the results of these measurements showed the wall thickness of the copper tube to be substantially the same as before its use. Only in the portion of the tube where the copper had been extremely hot due to the failure was there any indication of thinning.

Subsequent to this experimental work a spectrographic technique was worked out at the Ames Laboratory which permitted estimation of the ppm oxygen remaining in an yttrium fluoride sample. The samples from the three pressurized topping experiments were analyzed by this method and the results are shown in Table IV.
Table IV
Analyses of Yttrium Fluoride (Grade 3) Topped with Fluorine Gas at 20 PSIG.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>PPM oxygen</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>450, 380</td>
<td>415</td>
</tr>
<tr>
<td>08</td>
<td>520, 525, 450</td>
<td>498</td>
</tr>
<tr>
<td>09</td>
<td>290, 320, 290</td>
<td>300</td>
</tr>
<tr>
<td>002</td>
<td>330</td>
<td>330</td>
</tr>
</tbody>
</table>

The results tabulated in Table IV again indicate that the result of fluorine topping at room temperature is to increase the oxygen content of yttrium fluoride. This behavior remains unexplained. However, topping at temperatures in the 600°C range under a pressure of 20 psig does appear to be beneficial.

ESTIMATION OF HEAT OF REACTION AND FREE-ENERGY CHANGE FOR:
(A) THE FLUORINE-YTTRIUM OXIDE REACTION AND (B) THE HYDROGEN FLUORIDE-YTTRIUM OXIDE REACTION

In order to gain some idea of the amount of heat released by the fluorine-yttrium oxide reaction, thermochemical calculations were performed for the reaction

$$Y_2O_3 (s) + 3 F_2 (g) = 2 YF_3 (s) + 1.5 O_2 (g).$$  \(1\)
The calculations were made using data presented in Refs. (3) and (4).

The heat of reaction at any temperature $T$, $\Delta H_T$, was calculated using the relationship

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta C_p(T) dT \quad (2)$$

The heat of reaction at 298°K was calculated from estimated heat of formation data (4) and was found to be

$$\Delta H_{298} = -374,000 \text{ cal/mole } Y_2O_3 \quad (3)$$

The net heat capacity, $\Delta C_p(T)$, was determined in the usual manner. However, a discussion is in order concerning the heat capacity equations used for the various reactants and products.

The heat capacity at constant pressure for oxygen gas (4) was taken as

$$C_p(O_2) = 8.27 + 0.258 \times 10^{-3} T - 1.877 \times 10^5 / T^2 \quad (4)$$

Similarly, an expression for the heat capacity of solid yttrium oxide (4) was taken as

$$C_p(Y_2O_3) = 26.0 + 8.2 \times 10^{-3} T - 2.2 \times 10^5 / T^2 \quad (5)$$


(4) A. Glassner, Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°C, ANL-5750 (1957).
In this case the values were estimated by "use of analogy with compounds of neighboring elements in the Periodic Table."

The heat capacity at constant pressure for fluorine gas\(^{(3)}\) represented the heat capacity for the fluorine molecule considered as an ideal gas. These values were used rather than those given in Ref. \((4)\) because a plot of \(C_p\) versus the absolute temperature \(T\) revealed that the \(C_p\) values given \((4)\) fell below those presented \((3)\) for temperatures above 480°K. However, the heat capacity at constant pressure for an ideal gas, \(C_p^*\), should be smaller than that of a real gas. This can be shown rigorously, the difference being

\[
(C_p - C_p^*)_T = - \int_0^P T \left( \frac{\partial^2 \gamma}{\partial T^2} \right) dP.
\]

\((6)\)

Since an equation of state for fluorine gas was not available, recourse was taken to a plot of \((C_p - C_p^*)\) versus reduced pressure, \(P_R\), with parameters of constant reduced temperature, \(T_R\), as a means of applying corrections to the \(C_p^*\) data presented \((3)\). Such a plot appears in Hougen and Watson \((5)\). However, in the range of conditions for which we were interested, this correction never amounted to more than 0.05 calories per mole per °K and was consequently ignored in view of the considerable uncertainty of the data for the solid yttrium compounds involved.

The estimated value for the heat capacity at constant pressure for solid

yttrium fluoride was given\(^{(4)}\) as a constant 20 calories per mole per °K. When the net heat capacity, \(\Delta C_p\), for the reaction

\[
Y (s) + 1.5 \, F_2 (g) = YF_3 (s)
\]

was calculated using this value, it was found to decrease with increasing temperature, becoming negative at 700°K. But an estimated Eq. (4) for this same quantity showed it increasing with increasing temperature. Since \(C_p\) should, in general, increase with increasing temperature for a solid, it was decided to use this latter estimated equation for \(\Delta C_p\) to arrive at a more realistic estimation of the heat capacity of solid yttrium fluoride.

The estimated equation for \(\Delta C_p\) given in (4) was

\[
\Delta C_p = 1.4 + 8.3 \times 10^{-3}T + 1.2 \times 10^5/T^2 .
\]

An estimated equation for the heat capacity of solid yttrium metal\(^{(4)}\) was

\[
C_p(Y) = 5.6 + 2.2 \times 10^{-3}T .
\]

Using Eqs. (8) and (9) in conjunction with the \(C_p\) data for fluorine, as estimated equation for the heat capacity of solid yttrium fluoride was calculated as

\[
C_p(YF_3) = 19.3 + 11.6 \times 10^{-3}T - 0.035 \times 10^5/T^2 .
\]

Upon combination of the heat capacity data, an equation for the net heat capacity for the reaction denoted by Eq. (1) was found to be given by

\[
\Delta C_p(T) = 0.4 + 13.2 \times 10^{-3}T + 1.8 \times 10^5/T^2 .
\]
The free energy change for the reaction was determined from the relation
\[ \Delta F = -374,102 + 54.236T - 0.4T(\ln T) - 6.6 \times 10^{-3}T - 0.9 \times 10^5/T . \] (12)
This relation was derived from the defining equation for free energy. In addition to an equation for the net heat capacity and a value for the heat of reaction at one temperature, a value for the free energy change at a known temperature was required.

The free energy change at 298°K was calculated from estimated free energy of formation data \(^{(4)}\) and was found to be
\[ \Delta F_{298} = -359,500 \text{ cal/mole } Y_2O_3 . \] (13)

The use of Eq. (12) is restricted to a constant pressure of one atmosphere because of the similar restriction on the heat capacity. The heat of reaction and free energy change of reaction are tabulated in Table V for temperatures to 1000°K. Using the assumption that the free energy change previously calculated was the standard free energy change for the reaction at one atmosphere and the corresponding temperature, equilibrium constants were calculated for the yttrium oxide-fluorine reaction and are also presented in Table V.

Since it was now possible to calculate the thermochemical properties for the reaction between hydrogen fluoride and yttrium oxide, these calculations were performed in order to form a comparison between the two reactions. In this case, two reactions are possible. They are
\[ Y_2O_3 (s) + 6 HF (g) = 2 YF_3 (s) + 3 H_2O \] (14),
and
\[ Y_2O_3 (s) + 6 HF (g) = 2 YF_3 (s) + 3 H_2O (g) . \] (15)
Table V

Values Calculated for Heat of Reaction, Free Energy of Reaction, and Equilibrium Constant for the Reaction

\[ \text{Ti}_2\text{O}_3 (s) + 3 \text{F}_2 (g) = 2 \text{TiF}_3 (s) + 1.5 \text{O}_2 (g) \]

Taking Place at One Atmosphere.

<table>
<thead>
<tr>
<th>Temperature (^{\circ}\text{K})</th>
<th>Heat of reaction (cal/mole (\text{Ti}_2\text{O}_3))</th>
<th>Free energy of reaction (cal/mole (\text{Ti}_2\text{O}_3))</th>
<th>Equilibrium constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.16</td>
<td>-374,000</td>
<td>-359,500</td>
<td>(3.98 \times 10^{263})</td>
</tr>
<tr>
<td>400</td>
<td>-373,336</td>
<td>-354,647</td>
<td>(6.82 \times 10^{193})</td>
</tr>
<tr>
<td>500</td>
<td>-372,612</td>
<td>-350,056</td>
<td>(1.15 \times 10^{153})</td>
</tr>
<tr>
<td>600</td>
<td>-371,786</td>
<td>-345,622</td>
<td>(8.61 \times 10^{125})</td>
</tr>
<tr>
<td>700</td>
<td>-370,845</td>
<td>-341,333</td>
<td>(4.02 \times 10^{106})</td>
</tr>
<tr>
<td>800</td>
<td>-369,783</td>
<td>-337,187</td>
<td>(1.40 \times 10^{92})</td>
</tr>
<tr>
<td>900</td>
<td>-368,596</td>
<td>-333,184</td>
<td>(8.61 \times 10^{80})</td>
</tr>
<tr>
<td>1000</td>
<td>-367,282</td>
<td>-329,320</td>
<td>(9.93 \times 10^{71})</td>
</tr>
</tbody>
</table>
It was assumed that from 298°K to 373°K the water would come off as a liquid, while above 373°K water vapor would be expelled. The heat capacities for solid yttrium oxide and solid yttrium fluoride were given earlier. The heat capacity of hydrogen fluoride gas was taken\(^4\) to be

\[
C_p(\text{HF}) = 6.43 + 0.82 \times 10^{-3} T + 0.26 \times 10^5 / T^2.
\] (16)

The values of heat capacity for hydrogen fluoride at 400, 500 and 600°K appear suspect when compared to other reported values.\(^3\) However, Eq. (16) was taken to represent the heat capacity of hydrogen fluoride since the main area of interest was in the higher temperature regions where this equation yielded apparently reasonable results when compared with those reported.\(^3\)

The heat capacity of liquid water was taken to be a constant 18 calories per mole per °K. The heat capacity of water vapor was taken\(^6\) as

\[
C_p(\text{H}_2\text{O}) = 8.22 + 0.15 \times 10^{-3} T + 1.34 \times 10^{-6} T^2.
\] (17)

The latent heat of vaporization of water at one atmosphere was taken\(^7\) as 539.6 calories per gram.


The heat of reaction at 298°K was calculated from estimated heat of formation data and was found to be

$$\Delta H_{298} = -193,754 \text{ cal/mole Y}_2\text{O}_3.$$ \hfill (18)

The free energy change at 298°K was calculated from estimated free energy of formation data and was found to be

$$\Delta F_{298} = -141,600 \text{ cal/mole Y}_2\text{O}_3.$$ \hfill (19)

With this information, the heat of reaction and free energy change of reaction were calculated for the reactions denoted by Eqs. (14) and (15) and are presented in Table VI. Once again it was assumed that the free energy change so calculated was the standard free energy change for the reactions at one atmosphere and the corresponding temperature in order that equilibrium constants could be calculated.

A comparison of the figures presented in Tables V and VI shows the following: (1) the heat of reaction for the case involving HF is approximately half that for the case involving F2; (2) the free energy of reaction for the case involving HF is considerably less than that for the case involving F2, the release from the F2 reaction being approximately 2.5-4.5 times as large, depending on the temperature in question; and (3) the resulting equilibrium constant for the case involving HF is considerably less than that for the case involving F2.

**FLUORINATION OF YTTRIUM OXIDE**

To determine if the direct fluorination of yttrium oxide were feasible, several samples of yttrium oxide were fluorinated. The first experiment was conducted by turning on the fluorine with the reaction chamber at room temperature. The
Table VI

Values Calculated for Heat of Reaction, Free Energy of Reaction, and Equilibrium Constant for the Reaction

\[ \text{Y}_2\text{O}_3 (s) + 6 \text{HF (g)} = 2 \text{HF}_3 (s) + 3\text{H}_2\text{O} \]

Taking Place at One Atmosphere.

<table>
<thead>
<tr>
<th>Temperature (^\degree\text{F})</th>
<th>Heat of reaction(^a) (cal/mole Y(_2\text{O}_3))</th>
<th>Heat of reaction(^b) (cal/mole Y(_2\text{O}_3))</th>
<th>Free energy of reaction (cal/mole Y(_2\text{O}_3))</th>
<th>Equilibrium constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.16</td>
<td>-193,754</td>
<td>-193,754</td>
<td>-141,600</td>
<td>6.96 x 10(^{10})</td>
</tr>
<tr>
<td>373</td>
<td>-191,366</td>
<td>-162,228</td>
<td>-128,747</td>
<td>2.97 x 10(^{75})</td>
</tr>
<tr>
<td>400</td>
<td>-162,125</td>
<td>-162,125</td>
<td>-126,328</td>
<td>1.14 x 10(^{69})</td>
</tr>
<tr>
<td>500</td>
<td>-161,668</td>
<td>-161,668</td>
<td>-117,432</td>
<td>2.26 x 10(^{51})</td>
</tr>
<tr>
<td>600</td>
<td>-161,075</td>
<td>-161,075</td>
<td>-108,631</td>
<td>3.87 x 10(^{39})</td>
</tr>
<tr>
<td>700</td>
<td>-160,331</td>
<td>-160,331</td>
<td>-99,951</td>
<td>1.66 x 10(^{31})</td>
</tr>
<tr>
<td>800</td>
<td>-159,430</td>
<td>-159,430</td>
<td>-91,389</td>
<td>9.52 x 10(^{24})</td>
</tr>
<tr>
<td>900</td>
<td>-158,360</td>
<td>-158,360</td>
<td>-82,943</td>
<td>1.42 x 10(^{20})</td>
</tr>
<tr>
<td>1000</td>
<td>-157,114</td>
<td>-157,114</td>
<td>-74,512</td>
<td>1.96 x 10(^{16})</td>
</tr>
</tbody>
</table>

\(^a\) Water considered to be coming off as liquid.

\(^b\) Water considered to be coming off as vapor.
temperature rose to 242°C in 9 minutes and then began falling. The furnace was turned on at this time and the temperature gradually rose to 450°C over a period of 130 minutes. It was maintained at this temperature for the remaining 40 minutes of the three-hour experiment. The fluorine was then turned off and the sample cooled under nitrogen flow.

The remaining experiments dealing with direct fluorination of yttrium oxide were conducted without furnace heat. The variables investigated were particle size and the effect of time. It was observed that with the smaller apparent particle sizes, temperature rises of 44°C and 23°C were observed within the first 5 minutes of reaction, while with the larger particles a rise of only 1°C to 2°C was detected. An extremely thin bed was used for these room temperature experiments to minimize diffusion effects. The flow rate of fluorine was the same as that used earlier for the fluoride topping experiments.

The results of these experiments are presented in Table VII. Because of the high values obtained for the intensity ratio, only one measurement was made per sample. The data indicate that the size of the particle apparently has very little effect under the conditions studied. Conversion times of longer than three hours were not studied because intensity ratios of approximately unity can be obtained in this amount of time using anhydrous hydrogen fluoride gas.

The spontaneity of the reaction is such that it proceeds rapidly as soon as the fluorine comes into contact with the oxide. By observing the temperature-time relationships obtained it appeared that the major portion of the reaction was completed after approximately ten minutes. The fact that the reaction stops so far from equilibrium indicates that a resistance built up as a result
Table VII

Analyses of Yttrium Fluoride Produced by Fluorination of Yttrium Oxide at Atmospheric Pressure.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Conversion time (hr)</th>
<th>Conversion temperature (°C)</th>
<th>Depth of sample (in.)</th>
<th>Particle size</th>
<th>Intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-F ends</td>
<td>3</td>
<td>450</td>
<td>0.375</td>
<td>AR&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.92</td>
</tr>
<tr>
<td>11-F center</td>
<td>3</td>
<td>450</td>
<td>0.375</td>
<td>AR</td>
<td>2.6</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>25</td>
<td>UT&lt;sup&gt;b&lt;/sup&gt;</td>
<td>- 325 mesh&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.3</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>25</td>
<td>UT</td>
<td>- 325 mesh</td>
<td>2.7</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>25</td>
<td>-&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1/4-1/8 inch&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2.77</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>25</td>
<td>UT</td>
<td>60 mesh&lt;sup&gt;f&lt;/sup&gt;</td>
<td>2.78</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>25</td>
<td>UT</td>
<td>60 mesh&lt;sup&gt;f&lt;/sup&gt;</td>
<td>2.39</td>
</tr>
</tbody>
</table>

<sup>a</sup> Particle size distribution used as received.

<sup>b</sup> Depth of sample only a few particles deep at deepest point.

<sup>c</sup> Particles passed through 325 mesh Tyler screen.

<sup>d</sup> Sample consisted of large pieces of sample material spaced out.

<sup>e</sup> Material was used as received from calcining operation, i.e., unground.

<sup>f</sup> Particles retained on 60 mesh Tyler screen.
of reaction becomes dominant as the amount of conversion increases. It is difficult to envision what type of resistance this could be, however, since the particle size experiments were negative. Since the reaction is spontaneous, it would seem that the only thing which would be capable of slowing it down would be increased contacting difficulties. These in turn should lead to a significant difference when particles of widely different sizes are used.

If one were to assume that the reaction proceeds from the outside of the particle to the center, then diffusional difficulties through the reacted portion of the particle would or could conceivably come into play. However, one would expect the resistance to be proportional to the depth of the reacted portion. If one assumes that the reaction proceeds evenly, then the amount of unreacted material remaining in the core of a small particle should be smaller than the amount remaining in a larger particle. This difference would then be expected to be reflected in the intensity ratios obtained during subsequent analysis of the specimens but, as stated before, no such differences were detected.

This leads to the conclusion that the particles were actually very similar in size. It was observed during the screening of the oxide that there was a tendency for the particles to be broken up by shaking, to pass through the screen, and then to reagglomerate. Screen analyses made on the oxide showed that the material did not vary widely in particle size but the reliability of these screen analyses is subject to question on the basis of this type of behavior.

In view of this observation, the apparently contradictory results can be explained by assuming that the particles were actually very similar in size and
that the widely varying sizes of "particles" experimented with were actually nothing more than agglomerates of smaller particles. The mechanism controlling the rate of reaction would then be diffusion of the gases involved in the reaction into and out of these particles.

Since the resistance to gas flow between agglomerates would be small relative to the diffusion of the gas into the particle pores, the reaction would be expected to be rapid initially. As fluoride formed, the outer surface would be covered over with the solid fluoride product. During this formation period, the particle temperature would rise due to the large amount of heat generated by the reaction in a relatively short time. If the temperature became high enough to cause local melting of the fluoride, the fluoride could then be expected to flow into the pores leading to the interior of the particle and thus either increase the resistance to diffusion or, in the extreme case, plug the pore altogether. The net effect of this action would be to reduce the reaction rate and the observed conversion obtained in a given amount of time.

**FLUORINATION OF AN YTTRIUM OXIDE-YTTRIUM FLUORIDE BLEND**

The larger heat effect observed with direct fluorination of yttrium oxide was considered to be undesirable. In a large reactor, the rapid evolution of large amounts of heat could conceivably cause fusion within the bed, which could result in decreased conversion, possible vaporization of some of the fluoride produced, and also increased corrosion of the equipment. Possibly the best way to control this heat effect would be to dilute the reactants. By adding yttrium fluoride to the yttrium oxide, it was hoped to (1) control the
temperature by absorbing the heat in the additional mass supplied by the yttrium fluoride, (2) control the temperature without having to dilute the gaseous reactant, and (3) accomplish not only conversion of yttrium oxide to yttrium fluoride but also accomplish topping of the added fluoride. Earlier work by the author and co-workers (2) using anhydrous hydrogen fluoride gas and an yttrium oxide-yttrium fluoride blend showed the possibility of improving the conversion obtained per unit time.

This experiment was conducted under the same conditions as the first of the yttrium oxide experiments. A blend of two parts yttrium oxide to one part yttrium fluoride by weight was used.

The results of this experiment were not encouraging. The intensity ratio of the product was found to be 2.4. Previously (2) it had been demonstrated that it was possible to obtain intensity ratios of approximately 0.50 using anhydrous hydrogen fluoride gas at 600°C. On this basis, fluorination appeared to offer no advantages.

An interesting observation connected with this experiment was that while the temperature of the gas stream rose to 242°C in the first nine minutes when directly fluorinating the oxide, this temperature rose only to 135°C in eight minutes during the blend experiment. While the temperature rise was halved, the time factor remained approximately the same and the conversion obtained was about the same. It would appear from the assumptions concerning the mechanism of the reaction set forth in the preceding section that the inert fluoride material had a moderating effect on the temperature of the gas stream but that local temperatures were still becoming high enough to cause trouble.
The fluorination of yttrium chloride was tried also in an effort to obtain high purity yttrium fluoride. The chloride was prepared according to a procedure outlined by Mr. D. Dennison of the Ames Laboratory. A pyrex glass tube was used as the container for the reaction. A thermocouple enclosed in a glass thermowell was inserted into one end of this tube to measure the temperature. To this container were charged 37 grams of yttrium oxide, 43 grams of ammonium chloride, and 28.5 grams of hydroxylamine hydrochloride, all first ground together with a mortar and pestle.

The container was placed in a hinged combustion furnace used to supply heat. Helium flow was initiated through the container and heat applied. The temperature was brought to 350°C slowly over a period of 8 hours while a small flow of helium was maintained through the system. At the end of this time the resultant material was allowed to cool and was then extracted with absolute ethyl alcohol, previously dried over barium oxide in a desiccator. The filtration of the slurry proved to be a long, tedious process. The pale yellow solution which resulted was desiccated over barium oxide until used.

Twenty five milliliters of the solution was poured into an aluminum boat and placed in the fluorination chamber, which was now aluminum. Helium was passed through the system and the temperature was slowly raised to 100°C to remove the ethyl alcohol. The power input to the furnace was then turned off, the helium flow stopped, and fluorine flow started through the system under the customary conditions. During the first eight minutes, the temperature rose from an initial value of 117°C to 201°C. One-half hour after the start of the fluorination, the experiment was halted and the system was again flushed with helium. By this time the temperature had fallen to 122°C.

When the sample was removed it was observed that there was a large amount of very black soot contaminating both the reaction chamber and the top of the sample. Evidently not all the alcohol had been swept from the chamber before the fluorine was turned on and the subsequent rapid reaction resulted in free carbon being formed which deposited as soot. The sample appeared to be very white where it was not contaminated with soot. The purest sample available from this material was gathered. Duplicate analyses of the sample yielded intensity ratios of 0.94 and 1.67.
As can be seen, a lower intensity ratio was obtained by fluorinating yttrium chloride than by either of the other two procedures (fluorination of the oxide and fluorination of the oxide-fluoride blend). However, for the extra amount of labor involved in view of the results obtained, the method does not appear to offer much promise.

DISCUSSION AND CONCLUSIONS

None of the experiments reported herein yielded yttrium fluoride of the hoped-for purity. The fluorination of yttrium oxide and yttrium chloride were shown to be spontaneous processes which are exothermic. The only method of fluorination which could be termed partially successful was the topping of previously prepared fluoride material under what may be termed extreme conditions of temperature and pressure for a reaction involving the use of fluorine gas. A lesser degree of conversion was obtained when the topping was carried out at 25°C and one atmosphere pressure.

Thermochemical calculations were made using the best available data at the present time, and the results are presented. These results agree qualitatively with observed results in that the heat released by the fluorine reaction is considerably greater than that for the hydrogen fluoride reaction.

Because the heat released is much smaller in the case of the HF reaction, the undesirable exothermic effects resulting in the case of the F₂ reaction would be expected to be correspondingly moderated, and the results of past
experiments seem to indicate that they are. It is possible to obtain a much better conversion in a given amount of time using HF in spite of the fact that the driving force is considerably smaller. This fact can be related to the heat released in the following way. Assuming that the mass of absorbing solid is the same in each case, the smaller amount of heat liberated by the reaction will cause a lower resulting local temperature. Although there is evidence to indicate that the local temperatures do become high enough on occasion to cause some local melting of the fluoride product, this condition is not so severe as in the case of the fluorine reaction.

It appears possible with HF that the local temperatures will become hottest during the initial period of surface reaction and cause the bed to fuse at the points of mutual contact between adjacent particles. As the reaction proceeds into the interior of the particles, the heating effects are not so severe and the pores do not become clogged by fusing fluoride. Thus the rate of reaction depends to a greater extent on the concentration of the substances involved. In the case of fluorine, on the other hand, the rate of reaction not only depends on the concentration of the reactants but also upon the increasing resistance to diffusion being built up in the pores of the particle.

The lower equilibrium constant for the HF reaction means that the equilibrium conversion will not be as complete as for the case of the fluorine reaction. Using the equilibrium constant at 900°K given in Table VI, the
theoretical amount of oxygen remaining in the product material after equilibrium contact using the stoichiometric amounts of reactants was found to be 11 ppm. Experimentally, yttrium oxide hydrofluorinated at this temperature gave product material which contained about 300 or more ppm oxygen. For the fluorine reaction, the theoretical amount of oxygen remaining in the product material is found to be much less than one ppm for all temperatures investigated.

On the basis of the calculations made, it would appear that the lowest oxygen content yttrium fluoride could be prepared by the fluorine reaction if a way could be found to control the rate of heat release during reaction. The only workable method of accomplishing this appears to be to dilute the fluorine gas considerably. The main disadvantage of this approach is that the reaction time will necessarily be lengthened. However, it may be possible to reach a compromise such that the reaction time can be made reasonable and still produce a fluoride of acceptable purity.