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Bryan, William P.

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THE REACTIONS OF MIXED CRYSTALS OF
RARE EARTH FLUORIDES WITH FLUORINE GAS

William P. Bryan
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THE REACTIONS OF MIXED CRYSTALS OF RARE EARTH FLUORIDES WITH FLUORINE GAS

William P. Bryan
Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

August, 1957

ABSTRACT

The reactions of mixed crystals of rare earth fluorides with fluorine gas have been studied gravimetrically by determining the weight increases of mixed trifluoride samples upon exposure to fluorine at a pressure of 1 atmosphere and a temperature of 250°C. A special nickel helix balance was developed for directly studying these weight changes in an atmosphere of fluorine. The nature of the phases produced upon fluorination was studied by x-ray diffraction methods.

The following cerium-containing mixed trifluoride systems were studied over the whole range of compositions: CeF$_3$-LaF$_3$, CeF$_3$-YF$_3$, and CeF$_3$-PrF$_3$. In all these systems the cerium is completely oxidized to the $+4$ state, and in a restricted range of the CeF$_3$-PrF$_3$ system some of the praseodymium is oxidized to the $+4$ state.

The following terbium-containing mixed trifluoride systems were studied over the whole range of compositions: TbF$_3$-LaF$_3$ and TbF$_3$-YF$_3$. In neither case does complete oxidation of terbium to the $+4$ state occur after certain amounts of LaF$_3$ or YF$_3$ have been added to the TbF$_3$.

The above results are explained thermodynamically and the $\Delta F^{\circ}$ value for the reaction TbF$_3^+ 1/2 F_2 = TbF_4$ is estimated as being in the range between -278 calories and 0 calories at 250°C.
THE REACTIONS OF MIXED CRYSTALS OF RARE EARTH FLUORIDES WITH FLUORINE GAS

I. INTRODUCTION

A. Thermodynamic Discussion

One of the most interesting fields of study in modern inorganic chemistry involves the preparation and stability of unusual oxidation states of the various elements. The rare earth series of elements exhibits a striking uniformity of oxidation states. All the rare earths exist in the +3 state in stable compounds. In addition to the common +3 state, it is possible to prepare certain of the rare earths in the +2 or +4 states. Thus samarium, europium, and ytterbium can be prepared in the +2 state; and cerium, praseodymium, and terbium can be prepared in the +4 state. These unusual oxidation states are a result of the stabilities of the empty or nearly empty 4f electronic subshells in +4 cerium and +4 praseodymium; of the half-filled or nearly half-filled 4f subshells in +2 samarium, +2 europium, and +4 terbium, and of the completely filled 4f subshell in +2 ytterbium. In each case the elements tend to gain or lose electrons so as to achieve or nearly achieve these more stable electronic configurations.

The work presented herein was undertaken in order to study some aspects of the +4 rare earth fluorides and their stabilities. It is possible to illustrate the various factors involved in such stabilities by the consideration of a Born-Haber cycle. Such a cycle can be written in order to evaluate the thermochemical heat of formation of $\text{MF}_3$, where $\text{MF}_3$ refers to a rare earth fluoride.

$$
\begin{align*}
\text{UO}^{\text{MF}_3} & \rightarrow \text{M}^{+3} \quad + \quad 3\text{F}^- \\
\text{M}^{(s)} + 3/2\text{F}_2^{(g)} & \rightarrow \text{M}^{(g)} + 3\text{F}^{(g)}
\end{align*}
$$
In the diagram $Q_{\text{MF}_3}$ is the heat of formation of $\text{MF}_3$. $-Q_{\text{MF}_3} = \Delta H_{\text{r} \rightarrow \text{MF}_3}$. $U_0\text{MF}_3$ is the lattice energy of $\text{MF}_3$ at the temperature in question. $I_3$ is the energy required to remove three electrons from M. $E$ is the electron affinity of the fluorine atom ($\sim 84$ kcal/g at). $S$ is the heat of sublimation of M. $D$ is the dissociation energy of the $\text{F}_2$ molecule ($\sim 38$ kcal/mole). From the cycle it can be seen that we have

$$Q_{\text{MF}_3} = U_0\text{MF}_3 - I_3 + 3E - S - 3/2D. \quad (1)$$

In a similar manner it can be shown that we have

$$Q_{\text{MF}_4} = U_0\text{MF}_4 - I_4 + 4E - S - 2D, \quad (2)$$

where $U_0\text{MF}_4$ is the lattice energy of $\text{MF}_4$ and $I_4$ is the energy required to ionize four electrons from M.

Consider the reaction $\text{MF}_3 + 1/2 \text{F}_2 = \text{MF}_4$. The energy absorbed in this reaction, in terms of the aforementioned quantities, is simply the difference between the heats of formation of $\text{MF}_4$ and $\text{MF}_3$,

$$Q_{\text{MF}_3} - Q_{\text{MF}_4} = U_0\text{MF}_3 - U_0\text{MF}_4 + (I_4 - I_3) - E + 1/2D. \quad (3)$$

Note that $(I_4 - I_3)$ is the fourth ionization potential of M. The quantity $Q_{\text{MF}_3} - Q_{\text{MF}_4}$ must be low in order for tetrafluoride formation to be thermodynamically possible. Thus the higher $U_0\text{MF}_4$ and the lower the fourth ionization potential of M, the easier $\text{MF}_4$ formation becomes. Cerium and terbium form tetrafluorides because of the relatively low values of their fourth-ionization potentials.

Now consider the reactions of mixed crystals of rare earth trifluorides with fluorine. The mixed trifluoride can be written as $(M_I)_8(M_{II})_{1-8}\text{F}_3$, where $M_I$ and $M_{II}$ represent two rare earth metals. The mole fraction of $M_I\text{F}_3$ in the solid solution is $8\%$, and the mole fraction of $M_{II}\text{F}_3$ in the solution is $1-8\%$. This mixed trifluoride can react either by oxidation of $M_I$ alone or by oxidation of both $M_I$ and $M_{II}$. If one assumes complete oxidation, he can consider the first of these cases, thermodynamically, as occurring in three steps:

$$(M_I)_8(M_{II})_{1-8}\text{F}_3 = 8M_I\text{F}_3 + (1-8)M_{II}\text{F}_3, \quad (a)$$
\[ \delta M_{I} F_{3} + (8/2) F_{2} = \delta M_{I} F_{4} \quad (b) \]
\[ \delta M_{I} F_{4} + (1-\delta) M_{II} F_{3} = (M_{I})_{8} (M_{II})_{1-\delta} F_{3+8} \quad (c) \]

In order to determine the thermodynamic possibility of such reactions a constant pressure, the Gibbs free-energy change \( \Delta F \) must be considered. \( \Delta F \) for the above process is the sum of the \( \Delta F \)'s for the three steps:

\[ \Delta F = \Delta F_{a} + \Delta F_{b} + \Delta F_{c}. \quad (4) \]
\( \Delta F_{a} \) can be approximated if the assumption is made that \( M_{I} F_{3} \) and \( M_{II} F_{3} \) form an ideal solution. \( \Delta F_{a} \) is then the free energy absorbed in separating the ideal solution into its pure components:

\[ \Delta F_{a} = -[8 \text{ RT} \ln \delta + (1-\delta) \text{ RT} \ln (1-\delta)]. \quad (5) \]
\( \Delta F_{c} \) will be negative if the solid solution \( (M_{I})_{8} (M_{II})_{1-\delta} F_{3+8} \) is stable with respect to its components. Such a solution is far from ideal, so that \( \Delta F_{c} \) must be written in terms of activities:

\[ \Delta F_{c} = 8 \text{ RT} \ln a_{I} + (1-\delta) \text{ RT} \ln a_{II} \quad (6) \]

In this equation \( a_{I} \) and \( a_{II} \) are the activities of \( M_{I} F_{4} \) and \( M_{II} F_{3} \) in the solid solution. In the absence of any tendency toward intermediate-compound formation in such a solution, positive deviations from Raoult's Law will occur. Therefore \( a_{I} > \delta \) and \( a_{II} > (1-\delta) \). Thus \( \Delta F_{c} \) not only is negative but also has an absolute magnitude less than that of \( \Delta F_{a} \). The sum \( \Delta F_{a} + \Delta F_{c} \) then becomes a positive quantity. If \( \Delta F_{b} \) is negative, i.e., if \( M_{I} \) forms a tetrafluoride, then \( \Delta F \) can be either positive or negative. If \( \Delta F \) is negative then \( M_{I} \) can be oxidized, but if \( \Delta F \) is positive \( M_{I} \) cannot be oxidized in the mixed crystal even though it can be oxidized in the pure state.

In case both metals are completely oxidized the reaction can be written as the sum of four steps:

\[ (M_{I})_{8} (M_{II})_{1-\delta} F_{3} = \delta M_{I} F_{3} + (1-\delta) M_{II} F_{3} \quad (a) \]
\[ \delta M_{I} F_{3} + (8/2) F_{2} = \delta M_{I} F_{4} \quad (b) \]
Here it is possible to use the ideal-solution approximation for solutions of \( M_{\text{II}} F_3 \) and \( M_{\text{II}} F_3 \) as well as for solutions of \( M_{\text{I}} F_3 \) and \( M_{\text{I}} F_3 \). It can be seen that we have

\[
\Delta F_a + \Delta F_e \approx 0
\]

and

\[
\Delta F \approx \Delta F_b + \Delta F_d.
\]

In particular, note that even though \( \Delta F_a \) may be positive, \( \Delta F_b \) might be negative enough to make \( \Delta F \) negative and result in the thermodynamic possibility of the oxidation of both \( M_{\text{I}} \) and \( M_{\text{II}} \).

The assumption that \( M_{\text{I}} F_3 \) and \( M_{\text{II}} F_3 \) form ideal solutions will now be examined. There are two important criteria for ideal solutions. The first of these is that the change in volume on mixing is 0, i.e., \( \Delta V^m = 0 \). The second is that the heat or enthalpy of mixing is also 0, i.e., \( \Delta H^m = 0 \). Solid solutions of different rare earth trifluorides will be examined to see how well these two criteria are satisfied.

The unit-cell dimensions of solutions of various rare earth trifluorides in hexagonal \( \text{LaF}_3 \) have been measured by Schlyter.\(^1\) He found that the axial ratio \( c/a \) was constant for such solutions. The unit-cell volume and therefore the volume for one mole of \( M_{\text{I}} \text{LaF}_3 \) is then proportional to \( a^2 c \) or \( a^3 \). For \( \Delta V^m = 0 \), we have

\[
V = \delta V_M + (1-\delta)V_{\text{La}} = V_{\text{La}} - \delta(V_{\text{La}} - V_M),
\]

where \( V \) is the volume of 1 mole of final solution and \( V_{\text{La}} \) and \( V_M \) are the molar volumes of \( \text{LaF}_3 \) and \( M_F_3 \). In view of the above proportionality, we obtain

\[
a^3 = a_{\text{La}}^3 - (a_{\text{La}}^3 - a_M^3)\delta,
\]

where \( a_{\text{La}} \) and \( a_M \) are unit-cell dimensions for pure \( \text{LaF}_3 \) and \( M_F_3 \). Thus, if \( a^3 \) is plotted against \( \delta \), a straight line should result for \( \Delta V^m = 0 \).
In the treatment of his data Schlyter plotted $a$ against $\delta$ and obtained linear relationships for a number of different rare earth trifluorides dissolved in LaF$_3$. If $a^3$ is plotted against $\delta$, good straight lines are also obtained. Plots of $a^3$ against $\delta$ were made for the pairs CeF$_3$ - LaF$_3$, PrF$_3$ - LaF$_3$, and NdF$_3$ - LaF$_3$. In all these cases there was no discernible tendency away from linearity. In the other rare earth pairs studied, MF$_3$ has the orthorhombic structure; consequently complete miscibility of these fluorides with LaF$_3$ was not observed. Since the variation of $a$ is slight in these solid solutions the linearity of the $a^3$ - versus - $\delta$ plot cannot be regarded as a good test for solution ideality.

The volume change on mixing is not so sensitive a test for the ideality of a binary solid solution as is the enthalpy change. For any two real substances $\Delta H^m$ has some finite value. The problem is to estimate the value of $\Delta H^m$ and compare its magnitude with that of the free energy of mixing of an ideal solution. If the entropy of mixing is ideal, i.e., if the two components mix in a completely random manner, then the value of $\Delta H^m$ must be added to the ideal value of $\Delta F^m$ in order to obtain the real value of $\Delta F^m$.

In this discussion the entropy of mixing is assumed to be ideal. Some interesting results in regard to the entropies of mixing of similar ionic solids have recently been presented by McCoy and Wallace in their measurements of the entropies of mixing of KCl - KBr solid solutions. They found that the entropies of mixing were higher than the ideal values. Any ordering tendency in the solution would, of course, result in values lower than the ideal values. These higher values can probably be partially explained by the introduction of Schottky defects in the mixed crystals. Although these results do not rule out a certain amount of ordering tendency, it is probably safe to say that any ordering tendency becomes less as the similarity of the two components of an ionic solid solution increases. For substances of the same crystal structure, this similarity can be measured by the similarities of the unit-cell dimensions. The unit-cell dimensions for the fluorides of adjacent rare earths are very similar in value, so that the ordering tendency should be low and the entropy of mixing should be close to ideal.
Solid solutions of the alkali halides are the only ionic solid solutions whose heats of mixing have been extensively measured. In order to roughly approximate the heats of mixing of rare earth trifluoride pairs it is necessary to use these alkali halide data. It has been shown by Tobolsky \(^3\) that the heat of mixing of an equimolar solid solution of two alkali halides is roughly given by

\[
\Delta H^m \approx \text{const.} \frac{A_a}{a} \Delta^2,
\]

where \(A_a\) is the Madelung constant for the NaCl structure in terms of the unit-cell edge, \(a\) is the average size of the unit-cell edge for the alkali halides (\(\sim 6.5 \text{ Å}\)), and \(\Delta\) is defined as \(|100(a_2^2-a_1^2)/1/2(a_2^2+a_1^2)|\), the percentage difference between the unit-cell dimensions of the two pure components. Thus when \(\Delta H^m\) for solid solutions of alkali halides, in which 1/2 mole of each component is present, is plotted against \(\Delta^2\), a straight line should be obtained which should pass through the point \(\Delta^2 = 0, \Delta H^m = 0\). A plot of the experimental \(\Delta H^m\) values against \(\Delta^2\) was made, and a straight line was drawn through the points obtained. From this curve it is possible to estimate \(\Delta H^m\) for any two solids having the cubic NaCl structure, provided their unit-cell dimensions are known.

Equation (11) is applicable to any crystal structure if the proper Madelung constant is used. An approximate value for the Madelung constant of a rare earth trifluoride can now be obtained. The Madelung constant per valence bond, \(\alpha\), has an approximate value of about 1.6 for many different substances, \(^4\) and is given by

\[
\alpha = \frac{2A_Ro}{z_a z_c n},
\]

where \(A_{Ro}\) is the Madelung constant in terms of the shortest anion-cation distance, \(z_a\) and \(z_c\) are the anion and cation charges, and \(n\) is the number of atoms in the "molecule." For \(\text{LaF}_3\) or \(\text{YF}_3\) \(A_{Ro}\) would have an approximate value of 9.6. In \(\text{LaF}_3\), \(Ro\) is 2.4 Å, \(^13\) and in \(\text{YF}_3\), \(Ro\) is 2.3 Å. \(^14\) Therefore \(A_{Ro}/Ro\) for a rare earth trifluoride is about 4.2. For the alkali halides \(Aa\) is about 3.5 and \(a\) is about 6.5 Å, so that \(Aa/a\) is about 0.54.
In order to approximate $\Delta H^m$ values for rare earth trifluoride solid solutions, $\Delta$ values were estimated for these solutions. In the calculation of $\Delta$ values for hexagonal rare earth fluoride solutions, $\Delta$ was taken as the average of $\Delta a$ and $\Delta c$ for the two pure fluorides, where $\Delta a$ and $\Delta c$ have the same form as given above. For orthorhombic solid solutions $\Delta$ was taken as the average of $\Delta a$, $\Delta b$, and $\Delta c$.

Values of $\Delta H^m$ for the trifluoride solid solutions were estimated from the straight line drawn through the point $\Delta^2 = 0$, $\Delta H^m = 0$, and through the various experimentally measured values of $\Delta H^m$ for seven different alkali halide pairs, where $\Delta H^m$ corresponds to solid solutions containing 1/2 mole of each component. Values of $\Delta H^m$ corresponding to the $\Delta$ values for the rare earth trifluoride solid solutions were read from the curve and then multiplied by the factor $4.2/0.54 = 7.8$ in order to obtain $\Delta H^m$ values for rare earth trifluoride solid solutions. Estimates of $\Delta H^m$ values for various equimolar solid solutions are given in Table I. The experimental values for the alkali halide pairs in this table are: KCl-RbCl, 200 cal; KBr-KCl, 230 cal; NaCl-NaBr, 330 cal; KBr-KI, 390 cal.

Table I

<table>
<thead>
<tr>
<th>Pair</th>
<th>Structure</th>
<th>$\Delta$</th>
<th>$\Delta^2$</th>
<th>$\Delta H^m$ (cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl-RbCl</td>
<td>cubic</td>
<td>4.5</td>
<td>20.3</td>
<td>160</td>
</tr>
<tr>
<td>KBr-KCl</td>
<td>&quot;</td>
<td>4.8</td>
<td>23.0</td>
<td>180</td>
</tr>
<tr>
<td>NaCl-NaBr</td>
<td>&quot;</td>
<td>5.5</td>
<td>30.1</td>
<td>240</td>
</tr>
<tr>
<td>KBr-KI</td>
<td>&quot;</td>
<td>7.1</td>
<td>50.4</td>
<td>390</td>
</tr>
<tr>
<td>LaF$_3$-CeF$_3$</td>
<td>hexagonal</td>
<td>0.9</td>
<td>0.8</td>
<td>80</td>
</tr>
<tr>
<td>LaF$_3$-PrF$_3$</td>
<td>&quot;</td>
<td>1.5</td>
<td>2.3</td>
<td>160</td>
</tr>
<tr>
<td>LaF$_3$-NdF$_3$</td>
<td>&quot;</td>
<td>2.3</td>
<td>5.3</td>
<td>350</td>
</tr>
<tr>
<td>YF$_3$-ErF$_3$</td>
<td>orthorhombic</td>
<td>0.1</td>
<td>0.01</td>
<td>~ 0</td>
</tr>
<tr>
<td>TbF$_3$-YF$_3$</td>
<td>&quot;</td>
<td>1.2</td>
<td>1.4</td>
<td>115</td>
</tr>
<tr>
<td>GdF$_3$-TbF$_3$</td>
<td>&quot;</td>
<td>0.5</td>
<td>0.3</td>
<td>40</td>
</tr>
<tr>
<td>TbF$_3$-LuF$_3$</td>
<td>&quot;</td>
<td>2.2</td>
<td>4.8</td>
<td>310</td>
</tr>
</tbody>
</table>
The free energy of mixing of an ideal solution consisting of 1/2 mole of each component is -411 cal/mole at 298°C. From Table I it can be seen that the $\text{YF}_3-\text{ErF}_3$ solution is close to ideal and that solutions of adjacent rare earth pairs have $\Delta F^\text{m}$ values that are within ~10 to 20% of the ideal value. However, solid solutions of widely separated rare earths are not ideal.

B. Literature Survey

The various factors involved in the thermodynamic stability of the rare earth trifluorides and tetrafluorides, both pure and mixed, have now been considered. Previous work pertaining to these systems is summarized here. References are also given for the analogous rare earth oxide systems, since it is of interest to compare them with the fluoride systems.

The system Ca$_{2}O$ has been studied by Brauer and Gradinger and by Bevan. Ce$_{2}O_{3}$ is unstable in air, and the system is characterized by several intermediate phases between the two stoichiometric compositions. The system Pr$_2$O$_3$-PrO has been studied in some careful work by Eyring and co-workers. Again a number of nonstoichiometric phases are present in the complex system. Ordinary air ignition produces a phase of the composition Pr$_6$O$_{11}$. However, treatment of the lower oxides with O$_2$ at 282 atmos. and 400°C yields PrO$_2$. The Tb$_2$O$_3$-TbO$_2$ system has been studied by Gruen and co-workers. Three separate phases have been characterized in the region TbO$_1$-TbO$_{1.86}$. Treatment of Tb$_2$O$_3$ with O$_2$ at 282 atmos. and 400°C yields TbO$_{1.86}$. It is stated that TbO$_2$ can be produced by reaction of lower terbium oxides with atomic oxygen.

The rare earth trifluorides are characterized by two separate crystal structures, the LaF$_3$ or Tysonite type and the YF$_3$ type. The LaF$_3$ structure was first studied by Oftedal and later reinvestigated by
Schiyter, who assigned a simpler structure and smaller unit cell size to the hexagonal crystal. The YF$_3$ structure has been investigated by Zalkin and Templeton. YF$_3$ is orthorhombic. The hexagonal trifluoride is the stable form for elements from lanthanum to neodymium. The orthorhombic trifluoride is found for all elements from samarium to lutetium. However, the hexagonal form has also been produced for samarium, europium, holmium, and thulium; in fact, it seems likely that the hexagonal form is stable at elevated temperatures for all the elements from samarium to lutetium.

Cerium tetrafluoride is easily prepared from cerium trichloride and fluorine, or from cerium trifluoride and fluorine. The tetrafluoride is monoclinic and is isostructural with ZrF$_4$, HfF$_4$, ThF$_4$, UF$_4$, NpF$_4$, PuF$_4$, AmF$_4$, and TbF$_4$. The complex crystal structure of zirconium tetrafluoride has been determined by Burbank and Bensey.

Although Pr$_2$O$_3$ can be oxidized by heating in air, it has not been possible to oxidize PrF$_3$ by heating in F$_2$ or in ClF$_3$. Some calculations have been published by Perros and co-workers, who estimate that the free energy absorbed in the reaction PrF$_3 + 1/2$ F$_2 = $ PrF$_4$ is negative by at least 48 kcal/mole at 298 K. Thus one would predict that PrF$_4$ should be readily formed from PrF$_3$ and F$_2$. However, a more realistic calculation by Britton shows that the free-energy change for the above reaction is very close to zero; and in view of the lack of formation of PrF$_4$ under conditions in which CeF$_4$ and TbF$_4$ are formed, it seems reasonable to conclude that the free-energy change for the above reaction is slightly positive.

A recent report states that tetravalent praseodymium has been produced by fluorination of intimate mixtures of KF and PrF$_3$ at 550°C. The total fluorine content indicates an oxidation state of 3.5, and no x-ray lines characteristic of either PrF$_3$ or KF are present in the final product.

In contrast to the difficulties encountered in producing TbO$_2$, the production of TbF$_4$ is fairly easy if one starts with pure TbF$_3$ and heats in F$_2$ at 320°C. Terbium tetrafluoride is isostructural with CeF$_4$. X-ray powder-diffraction data for TbF$_4$ have been given by Templeton and Daubin.
Previous experimental results relating to the oxide and fluoride systems of pure rare earths having both a +3 and +4 oxidation state have now been given. Next, similar results on mixed rare earths will be presented. A number of studies have been made on mixed-oxide systems in which one of the components crystallizes in the fluorite structure. Thus the system CeO$_2$-LaO$_3$ has been studied by Zintl and Croatto; the systems CeO$_2$-Nd$_2$O$_3$, CeO$_2$-Pr$_2$O$_3$, and PrO$_2$-Nd$_2$O$_3$ have been studied by McCullough; the systems CeO$_2$-Sm$_2$O$_3$, CeO$_2$-Gd$_2$O$_3$, CeO$_2$-Y$_2$O$_3$, and PrO$_2$-Y$_2$O$_3$ have been studied by McCullough and Britton; and the systems CeO$_2$-Y$_2$O$_3$, CeO$_2$-Sm$_2$O$_3$, and CeO$_2$-Yb$_2$O$_3$ have been studied by Brauer and Gradinger. All these systems show a region in which the sesquioxide is dissolved in the dioxide to produce a fluorite phase in which anion vacancies are present, as shown by the relative intensities of x-ray diffraction lines and the correlation of density measurements with lattice constants.

In contrast to the amount of work done on rare earth mixed-oxide systems, the studies on mixed fluoride systems have been meager. The work of Schlyter on the unit-cell dimensions of solutions of rare earth trifluorides in LaF$_3$ has already been mentioned. Schlyter and Sillen have studied the coprecipitation of certain tetravalent ions with LaF$_3$. In particular it was found that as much as 44% CeF$_4$ can dissolve in LaF$_3$ when both the La$^{+3}$ and Ce$_{4+}$ ions are coprecipitated from solution. From x-ray data the authors deduce that cation vacancies are produced when the LaF$_3$ structure takes up CeF$_4$. The F$^-$ lattice is thought to be unchanged.

As can be seen from the foregoing summary of previous work, there have been no thermodynamic studies involving the higher rare earth fluorides. Further, the equilibrium involved in the reaction MF$_3$ + $1/2$ F$_2$ = MF$_4$ has not been investigated thermodynamically. The original object of this work was to study this equilibrium. In the course of preliminary attempts to oxidize some impure terbium preparations it was found that under conditions sufficient to oxidize pure TbF$_3$ it was impossible to oxidize TbF$_3$ containing only a few percent of other rare earth fluorides as impurities. This interesting effect appeared worthy of further study. In addition, the large amount of work on mixed rare earth oxide systems
points up the lack of data on the equally interesting mixed fluoride systems. The differences observed in the stabilities of the higher oxides and fluorides of praseodymium and terbium also indicate the need for further studies on the higher rare earth fluorides.

With these considerations in mind the decision was made to study selected rare earth trifluoride solid solutions and their reactions with $F_2$ gas. This thesis presents the results of such an investigation.
II. EXPERIMENTAL APPARATUS AND METHODS

A. Purity of Reagents

All the rare earths used in this work were analyzed spectroscopically by John Conway's group in this laboratory. The La$_2$O$_3$ was obtained from Lindsay Light and Chemical Co. and contained < 0.03% calcium, < 0.02% aluminum, and < 0.03% iron. No other rare earths were detected. The source of cerium was G. Frederick Smith reference-purity ammonium hexanitrato cerate. This material was found to be free from other rare earths and to contain traces of iron, aluminum, and vanadium. The Y$_2$O$_3$ was obtained from Research Chemicals Inc. and contained 0.01% aluminum, 0.03% iron and no detectable rare earths. Praseodymium oxide obtained from Research Chemicals Inc. had no spectroscopically detectable impurities. Terbium oxide was obtained from Mitten Chemicals; all impurities in this sample were below the spectroscopic limits of detection.

B. Preparation of Mixed Fluorides

Stock solutions of La$^{3+}$ and Y$^{3+}$ were prepared by dissolving approximate amounts of La$_2$O$_3$ and Y$_2$O$_3$ in dilute nitric acid. The solutions were then analyzed by adding known volumes to weighed platinum plates, drying the plates under a heat lamp, and igniting the plates to constant weight with an induction heater. The ignited products were weighed as La$_2$O$_3$ and Y$_2$O$_3$. The Ce$^{3+}$ stock solution was prepared by dissolving ammonium hexanitrato cerate in water and adding hydroxylamine hydrochloride until reduction was complete, as evidenced by the disappearance of the characteristic orange color of the hexanitrato cerate ion. The solution was analyzed by ignition as described above, the ignited product being weighed as CeO$_2$. Praseodymium oxide was dissolved in HCl and analyzed by its absorption spectrum, using a Beckmann D. U. Spectrophotometer. The Tb$^{3+}$ stock solution was prepared by reducing "Tb$_4$O$_7$" in a stream of H$_2$ at 600° to 700° for 1.5 hours. Weighed quantities of the Tb$_2$O$_3$ produced
were then dissolved in a mixture of HNO$_3$ and HCl and diluted to known volume with water.

Solid solutions of the mixed rare earth fluorides were prepared by thoroughly mixing known volumes of stock solutions of the two rare earths desired and then adding an excess of concentrated HF. The Ce-La, Ce-Y, and Ce-Pr solid solutions were precipitated in platinum cones. The Tb-La and Tb-Y solid solutions were precipitated in fluorothene cones. All the precipitates were then washed three times with dilute HF, which prevents peptization, and then dried. The cerium containing solid solutions were dried overnight in glass tubes at 150°C in a glass vacuum manifold, which was evacuated by means of a Duoseal vacuum pump. Because only a small amount of terbium was available it was found convenient to dry the terbium-containing solid solutions in the cones in which they were precipitated. Therefore overnight drying was conducted at room temperatures. The same vacuum manifold and pump were used.

In order to remove all water from the fluoride solid solutions, further drying was necessary. Therefore, after the above preliminary drying, the solids were powdered in an agate mortar and added to glass tubes that had closed bottoms and were plugged with glass wool on top. These tubes were inserted in large quartz tubes which were attached by means of standard taper joints to a glass manifold which could be inserted into a high-vacuum line. The quartz tubes were heated by nichrome-wound ceramic heaters. All mixed fluoride solid solutions were heated overnight in high vacuum at approximately 500°C by means of this arrangement. X-ray powder patterns of these heated and vacuum-dried materials revealed no traces of oxyfluorides or oxides. It was assumed that these vacuum-heated materials, which were nonhygroscopic, consisted only of mixed trifluorides.

C. The Nickel Helix Balance

In order to determine the extent to which the mixed fluorides reacted with F$_2$, it was necessary to have some method of measuring the weight gain of the solid sample upon exposure to a fluorine atmosphere.
Nickel, with a thin protective coating of nickel fluoride, is known to be resistant to attack by fluorine at temperatures below about 300° to 400°C. An all-nickel apparatus was constructed, with the intention of determining the equilibrium constant of the reaction \( MF_3 + \frac{1}{2} F_2 = MF_4 \) by observing the gain or loss of weight (gain, \( MF_3 + \frac{1}{2} F_2 \rightarrow MF_4 \); loss, \( MF_4 \rightarrow MF_3 + \frac{1}{2} F_2 \)) of a fluoride sample as a function of temperature at fixed \( F_2 \) pressure. Although attempts to measure the \( CeF_3-CeF_4 \) equilibrium were unsuccessful because of the low partial pressures of \( F_2 \) over CeF₄ at temperatures suitable for use of the nickel apparatus, the apparatus did serve to give a quantitative measurement of the weight gain of the solid trifluoride samples upon exposure to \( F_2 \) below temperatures of about 400°C.

The apparatus was very simple in principle and is illustrated in Fig. 1. It consisted of a long closed vertical nickel tube in which a nickel wire, the upper portion of which was wound in the form of a helix, was suspended. The lower portion of the wire was straight, and a nickel pan containing the sample was suspended from the end of the wire. The lower portion of the tube could be heated to a temperature sufficient for the sample to react. Thus the apparatus was simply a spring balance designed to operate in a fluorine atmosphere. Provision was made for the visual observation of the deflection of the spring balance by means of markers on the wire below the helix viewed through fluorine-resistant windows built into the wall of the tube.

The tube or balance case was made from a piece of stock 1-inch-diameter nickel tubing which was 2.5 feet long. The bottom of the tube was closed off by means of a nickel disc welded to the bottom. The top of the tube was threaded on the outside so that a nickel screw cap could be screwed onto the tube. This screw cap was equipped with a small hook welded to its underside on which the helix could be hung. Two 1/2-inch-diameter nickel side-arm tubes were welded to opposite sides of the balance case about 10 inches down from the top. These tubes were threaded on the outside so that window holders could be screwed onto the case. Light could be admitted through one window and observations could be made through the other window. About 3 inches further down the tube a
MOM
TH ER M 0 CO I
WELL
F2 INLET
REW CAP
LIX
JDO W TUBE
RKER LOOPS
F2 OUTLET
INGDOWN
IRE
NICKEL HELIX BALANCE
(NOT TO SCALE)

SCREW CAP
HELI X
WINDOW TUBE
MARKER LOOPS
HANGDOWN WIRE
PAN

Fig. 1.
thermocouple well made of 1/8-inch nickel tubing was welded to the side of the tube. This well was closed at the bottom and ran parallel to the axis of the balance case along the inner side of the case. An iron-constantan thermocouple was inserted into this well so that the end of the thermocouple was close to the position of the pan during balance operation. Three inches below the thermocouple-well outlet, 1/4-inch gas inlet and gas outlet tubes were welded to the balance case. The gas-inlet tube ran down the inside of the balance case parallel to the thermocouple well and ended close to the case bottom. Both the inlet tube and the thermocouple well were held to the nickel case by means of a heavy nickel wire welded to the case. Thus these tubes could not interfere with balance operation. Inlet and outlet tubes were equipped with brass flare fittings for attachment to the rest of the fluorine line.

The helix was made from 5-mil nickel wire hand-wound on a 3/8-inch-diameter metal rod. The helices used usually had about 70 turns. A 3-mil nickel wire was attached to the bottom of the helix and acted as a straight hang-down wire from which the pan was suspended. A number of small loops were made along the upper portion of this wire. These closely spaced loops served as markers and could be observed through the windows when the balance was loaded.

The balance pans were made from 1-mil nickel foil. A rectangular piece of foil was wrapped in the form of a cylinder and the seam was carefully spot-welded. Then a bottom piece was carefully spot-welded to one end of the cylinder. Two holes were punched near the other end of the cylinder to accommodate a nickel suspension wire. By this means the pan could be hung from a hook formed at the end of the hang-down wire. The pans were weighed from 50 to 80 milligrams and could easily hold 200-milligram samples of mixed fluorides without danger of spilling.

The windows were made from pieces of transparent fluorethene plastic. These windows were not attacked by \( \text{F}_2 \) and completely retained their transparency, even after numerous exposures to fluorine. The window holders were made from circular pieces of nickel 1.5 inches in
diameter and 1/2 inch thick. Holes were drilled part way through the centers of these pieces and tapped so that these circular pieces could be screwed onto the window-holder side arms. Slightly smaller holes were then drilled the rest of the way through the window holders. This left a ridge which accommodated a soft copper gasket placed between the window holder and window-holder side arm. Four small holes were drilled around the outsides of the window holders and corresponding holes were drilled in a flat outer ring made of 0.05-inch brass sheet. The windows could then be inserted between the holders and the outer rings, and the whole assembly could be bolted together by means of bolts passing through the small holes. The inner sides of the windows were sealed to the nickel window holders by means of Permatex-2 gasket cement.

In measuring the reliability of the spring balance two factors must be considered. First, does the sensitivity of the balance remain constant during exposure to fluorine; and second, does the balance pan, which is in the lower portion of the tube and therefore exposed to hot F₂, remain constant in weight after it has a protective NiF₂ coating?

Before each run the balance sensitivity was measured by observing the rest point of one of the marker loops before and after a platinum wire of known weight was hung on the already loaded pan suspended from the hang-down wire. A special glass case was constructed so that this operation could be carried out outside the nickel tube and away from air currents. The rest points were measured by means of a short-range cathetometer accurate to 0.001 mm.

Sensitivity results on one particular helix, which was used repeatedly, gave values in the range 0.308-0.317 mm/mg. This helix was used throughout an entire year. In general, if the helix remained unused for several days, lower values for the sensitivity were obtained. Higher values were obtained if the helix was reused only shortly after a previous run. The sensitivity was always in the above range and appeared to be a function only of length of time the helix had been exposed to air before sensitivity measurement.
The constancy of pan weight was very satisfactory. After several heatings in a $F_2$ atmosphere empty pans could be heated to temperatures of 400°C in $F_2$ gas at 1 atmos. pressure and remain constant in weight to the nearest 0.01 mg.

D. Methods Used in Fluorination Runs

The fluorine gas used in this work was obtained in a large cylinder from the General Chemical Corp. The cylinder contained 6 lb of $F_2$ at a pressure of 400 psi. The gas was transferred to a smaller cylinder of convenient size by means of a line made from brass pipe fittings. Permatex-2 gasket cement was used as luting. The line was equipped with two heavy Hoke O. K. metal needle valves and a brass Burdon gauge of 1000 psi capacity. The Kerotest valve, which has teflon packing, should not be used in such a system because teflon and fluorine react at high pressure. The smaller cylinder was pre-evacuated by means of a Cenco Hi Vac pump filled with fluorocarbon oil, and then $F_2$ was carefully transferred into the smaller cylinder until a pressure of about 80 psi was obtained there. This smaller cylinder was used as a $F_2$ source in the $F_2$ line described below. In handling $F_2$ at 400 psi it is essential that all pipe fittings be extremely tight and that ordinary screw thread fittings be protected by soft copper gaskets. The line should be pre-tested for leaks by filling it with $F_2$ at about 1 atmos. pressure and testing all connections with ammonia water. Small explosions and white ammonium fluoride fumes indicate the presence of a leak.

The fluorine line used in the fluorination experiments is shown in Fig. 2. It was made from 1/4-inch-diameter nickel tubing and brass pipe fittings. Connection between the nickel tubing and brass fittings was made by means of flare fittings. Permatex-2 gasket cement was used as luting for the pipe fittings. The gas cylinder was closed off from the rest of the line by several heavy Hoke O. K. valves. A nickel trap containing solid KF, to remove HF from the $F_2$, was inserted in the line between the balance case and the valves. Several brass Bourdon gauges
Fig. 2.
were inserted in the line to measure the $F_2$ pressure at various points. One of these gauges was a compound gauge so that evacuation of the line could also be measured. The line could be evacuated through a small Hoke valve by means of a Hi Vac pump filled with fluorocarbon oil or by means of a water aspirator emptying into a hood. The pump and aspirator could be connected to the line by 1/4-inch-diameter soft copper tubing.

The procedure used in making a fluorination run using the helix balance was as follows.

First an empty nickel pan was weighed on an Ainsworth Microbalance to the nearest 0.01 milligram. Then an ~100-mg sample of mixed fluoride was added to the pan, which was again weighed. The pan was then hung from the helix, which was attached to the nickel balance-case screw cap. The loaded balance was then placed in the glass calibration case, the cap being supported by means of glass indentations in the case. The bottom of the glass case could be removed so that a platinum wire weight could be hung directly onto the pan. The rest point of one of the marker loops was read with the cathetometer and then the weight was added to the pan, after which the new rest point was taken. Sensitivity was measured in millimeters per milligram. The sensitivity used in a run was taken as the average of at least two separate sensitivity determinations made before each run.

After sensitivity determination the helix and pan were placed in the nickel balance case, which was already attached to the fluorine line. The cap was screwed down tight. It was now possible to observe marker loops through the windows, and these loops were checked to see that the pan was hanging freely. If the pan is free the loops have a characteristic bobbing motion when the balance case is given a slight upward push. The same cathetometer used in sensitivity determination was then set up to observe a convenient marker loop. The marker loops were illuminated by shining a microscope lamp through the window.

The line was then evacuated, after which $F_2$ was slowly passed in until a pressure of 1 atmos. was attained. The marker position was then read. The lower portion of the balance case was then slowly heated
be means of a cylindrical resistance wire heater operated through a variable transformer. Heat conduction to the upper portion of the case was minimized by cooling the case just above the heater by means of an air jet. Marker readings were taken at convenient intervals. When a temperature of 250°C was reached, as measured by an iron-constantan thermocouple in the thermocouple well, further heating was stopped, and the temperature was allowed to remain at 250°C during the rest of the experiment. Readings were taken until a constant value was obtained over a long period of time or until long after the reaction appeared to be over. At times no constant value was reached. In these cases a slow apparent weight increase was observed with time. Correction was made for this drift by extrapolating the drift points and subtracting this drift from the over-all balance deflection.

A representative plot of such an experiment is given in Fig. 3, where cathetometer readings are plotted against time. This particular experiment consisted of heating a mixed fluoride containing 26.4 mole % CeF₃ and 73.6 mole % YF₃ in 1 atmos. of F₂ at 250°C. The sample weighed 96.47 mg. The sample therefore contained 32.66 mg of CeF₃. If all the CeF₃ present were converted to CeF₄, a weight gain of 3.14 mg should be observed. The balance sensitivity was 0.314 mm/mg, so that a balance deflection of 0.314 x 3.14 or 0.99 mm should be observed.

Since the cathetometer telescope inverts the marker image, a decreasing reading corresponds to an increasing weight, and the loop has an apparent upward motion in the field of view. As can be seen from Fig. 3 there is an initial weight loss before the start of the reaction. This is probably due to the loss of traces of water from the sample while it is being heated. The maximum point on the curve was taken as the initial deflection reading. From the shape of the curve it appears that the reaction takes about 3 hours to go to completion. After the reaction is over there is a linear drift. By extrapolating this drift back to the time of maximum reading, the final deflection reading was obtained. The initial deflection reading is 9.07 mm; the final deflection reading is 8.11 mm. The balance deflection is then 0.96 mm, and corresponds to 0.96/0.99 or 98% oxidation of the cerium present in the sample.
Fig. 3. Cathetometer reading vs. time for fluorination of 26.4% CeF$_3$ - 73.6% YF$_3$ mixed trifluoride.
After the heating period the sample was allowed to cool in $F_2$. The $F_2$ was then pumped out of the balance case and the helix and pan were removed. The pan was then reweighed on the microbalance. Thus the weight gain of the pan contents could be determined both by balance deflection and by before-and-after weighing of the pan itself. In the particular experiment described above the pan contents gained 3.06 mg in weight, corresponding to $3.06/3.14 = 97.5\%$ oxidation of the cerium present.

The helix balance was used in the experiments with the $\text{CeF}_3$-$\text{LaF}_3$, $\text{CeF}_3$-$\text{YF}_3$, and $\text{CeF}_3$-$\text{PrF}_3$ systems. Because the quantities of terbium available were smaller, a different method had to be used in measuring the weight gains of the $\text{TbF}_3$-$\text{LaF}_3$ and $\text{TbF}_3$-$\text{YF}_3$ systems upon exposure to $F_2$. Here the average-sized mixed-fluoride sample was such that a weight gain of about 0.1 mg would correspond to complete oxidation of the terbium.

The reaction chamber used in the terbium experiments is shown in Fig. 4. It consisted of a piece of 1-inch-diameter nickel tubing about 1 foot long. The outer ends of the tube were threaded and hexagonal screw caps constructed to fit over the ends. The screw caps and tube ends were sealed by means of soft copper gaskets. Each screw cap had a 1/4-inch-diameter tube welded to its center in order to provide inlet and outlet passages for the fluorine. The reaction chamber could be attached directly to the fluorine line by means of flare fittings. The central portion of the reaction chamber was wrapped with asbestos and then a nichrome resistance heater was wound over the asbestos. A thermocouple was inserted between the outside of the tube and the heater and insulated from the tube and heater by means of asbestos. The heater was then wrapped with asbestos. From a calibration of the outer thermocouple reading against a thermocouple inside the reaction chamber it was possible to obtain the temperature inside the reaction chamber from the reading of the outer thermocouple.

The same nickel pans described previously were used to hold the fluoride samples. These pans were held in a nickel block which could be inserted into the reaction chamber. The experimental procedure was to
SCREW CAP
HEATER

BLOCK WITH SAMPLE PANS
OUTER THERMOCOUPLE

TO PUMP

Fig. 4.
take known weights of mixed trifluorides and heat them at 250°C and in 1 atm. of fluorine until they came to constant weight. The samples were weighed to the nearest 0.01 mg. The degree of oxidation could then be calculated from the sample weight gain.

E. Conversion of Fluorides to Oxides

The reactions of mixed fluorides of CeF$_3$ and LaF$_3$ with F$_2$ were the first group of the mixed-fluoride reactions to be studied. In order to test the reliability of the previously described methods, the amount of cerium oxidation in the CeF$_3$-LaF$_3$ system was determined by converting the fluorination products to oxides. Weighed samples of fluorination products were heated in air to constant weight in small pans made from platinum foil. Heating was conducted at about 800°C in a muffle furnace.

It was assumed that any CeF$_3$ or CeF$_4$ in the samples was converted to CeO$_2$ and that all LaF$_3$ was converted to La$_2$O$_3$. The amounts of CeF$_4$ and CeF$_3$ in the fluoride samples were calculated by solving the following simultaneous equations:

$$\frac{x}{2} (\text{CeO}_2) + \frac{y}{\text{La}_2\text{O}_3} = \delta,$$

$$z + w + \left[ \frac{2 (\text{LaF}_3)}{\text{La}_2\text{O}_3} \right] y = I,$$

$$\left( \frac{\text{CeO}_2}{\text{CeF}_4} \right) z + \left( \frac{\text{CeO}_2}{\text{CeF}_3} \right) w = x.$$

In these equations

$\delta$ is the mole fraction of CeF$_3$ in the original trifluoride sample,

$I$ is the initial weight of fluorinated fluorides,
F is the final weight of oxides, 
\[ x \] is the weight of CeO_2 produced,
\[ y \] is the weight of La_2O_3 produced,
\[ z \] is the weight of CeF_4 present in the fluorinated material,
and \[ w \] is the weight of CeF_3 in the fluorinated material.
The chemical formulas represent molecular weights. The percentage of cerium oxidized in a given fluorination run was then calculated from the expression:

\[
\text{Percent cerium oxidized} = 100 \frac{z/CeF_4}{z/CeF_4 + w/CeF_3}
\]

If the weight gains on fluorination are greater than those corresponding to complete conversion to tetrafluoride, solution of the above equation gives negative values for \( w \). Several such cases were observed at values of \( \delta < 0.55 \). In such cases it was assumed that the extra weight gain was due to extra fluorine being taken up by the fluorinated material. This assumption enables the calculation of results on the same basis as those calculated from helix deflections and weight changes on fluorination. The following equations were used in these calculations:

\[
x + y = F,
\]

\[
\frac{x/2 \text{ (CeO}_2\text{)}}{x/2 \text{ (CeO}_2\text{)} + y/\text{La}_2\text{O}_3} = \delta.
\]

\[
\left(\frac{\text{CeF}_4}{\text{CeO}_2}\right) x + u + \left[\frac{2 (\text{LaF}_3)}{\text{La}_2\text{O}_3}\right] y = I
\]

\[
\left(\frac{\text{CeF}_4}{\text{CeO}_2}\right) x = z
\]

Here \( u \) represents the weight of extra fluorine taken up during fluorination. The percent of cerium oxidized was then calculated as

\[
\text{Percent cerium oxidized} = 100 \left( 1 + \frac{u/19.0}{\delta/CeF_4} \right).
\]
F. Methods Used in X-Ray Determinations

The nature of the phases present in the mixed fluorides before and after reaction with fluorine was investigated by means of x-ray diffraction powder photographs. Cameras of 5 cm radius were used with copper Kα radiation. The wave length of this radiation was taken as 1.5418 Å. The powder samples were held in pyrex capillaries. Many of the samples were poorly crystallized, especially the fluorinated samples in which reaction had occurred, since in these cases large numbers of lattice defects were present. Consequently it proved impossible to calculate accurate unit-cell dimensions from photographs of these samples. In many cases only a few lines of low θ could be observed on the films. The high θ lines, which are more sensitive to changes in unit-cell dimensions, could not be read from the films. Although these photographs were not good enough for accurate unit-cell dimension calculations, they were used to identify the phases present.

In order to calculate unit-cell dimensions for some of the better crystallized samples, a method was developed which made use of a North American Phillips Co. Norelco Wide Range Goniometer. This instrument is a wide-range Geiger counter x-ray spectrometer, and consists of a geiger tube designed to rotate about a rotating flat sample at twice the rate of sample rotation. Thus the Geiger tube always makes an angle of 2θ with the undiffracted x-ray beam. The signal from the Geiger tube is fed through conventional circuits and recorded on a scaler and a Brown Recording Potentiometer. The potentiometer gives a plot of x-ray intensity against θ. From this plot it is possible to get precision θ values for the various diffraction lines, provided the instrument is accurately calibrated.

In calibrating the instrument it was decided to mix the fluoride samples with some material that had accurately known θ values. CeO₂ was chosen for this purpose since it has convenient diffraction lines and since a large quantity of very pure CeO₂ was available. An x-ray diffraction photograph of this material was taken on a large camera of 11.4 cm radius. This excellent photograph was used to get a precision unit-
cell dimension for cubic CeO$_2$. Corrections were made for film shrinkage in the measurement of $\theta$ values. In the cubic system $\sin^2 \theta$ is equal to $\lambda^2/4a^2 (h^2 + k^2 + l^2)$. A plot of $\sin^2 \theta/(h^2 + k^2 + l^2)$ was made against $\sin^2 \theta$, and the curve was extrapolated to $\sin^2 \theta = 1$. The value $a = 5.411$, which agrees with the value obtained by McCullough, was calculated from this extrapolated value of $\lambda^2/4a^2$. From this value of $a$, it was possible to calculate accurate values of $\theta$ for all the CeO$_2$ diffraction lines. These $\theta$ values were used as calibration points in the measurements with fluoride samples.

Each fluoride sample was prepared by spreading collodion solution in the form of a small rectangular patch on bond paper. A mixture of fluoride and CeO$_2$ was then taken up in a collodion slurry and spread onto this patch. After the collodion was dry these patches could be removed from the paper and pressed overnight between microscope slides. The flat samples then consisted of fluoride and CeO$_2$ held in a collodion sheet. The samples were then taped to the aluminum sample holders of the Norelco Goniometer and run for $\theta$ values from about $10^\circ$ to $30^\circ$. This limited range was used because no good fluoride peaks could be obtained above $30^\circ$. The CeO$_2$ peaks obtained were well defined, and permitted the accurate determination of a $\theta$ scale for each plot.

Unfortunately the fluoride peaks were very poor, owing to the lack of good crystals and to the presence of lattice defects. This was especially true when reactions had occurred on fluorination. Materials having the monoclinic CeF$_4$ structure gave no detectable peaks, so that it was not possible to obtain unit-cell dimensions for these materials. Peaks were obtained for a few of the prominent low lines for fluorides having the hexagonal LaF$_3$ and orthorhombic YF$_3$ structures. These peaks were often barely above noise level and were ill defined.

The peaks obtained were indexed by means of the data given by Schlyter for LaF$_3$, and Zalkin and Templeton for YF$_3$. Unit-cell dimensions were calculated from the formulas

$$\sin^2 \theta = \frac{\lambda^2}{3a^2} (h^2 + hk + k^2) + \frac{\lambda^2}{3a^2} l^2$$

for the hexagonal fluorides,
\[ \sin^2 \theta = \frac{\lambda^2 h^2}{4a^2} + \frac{\lambda^2 k^2}{4b^2} + \frac{\lambda^2 l^2}{4c^2} \]

for the orthorhombic fluorides.

In the hexagonal fluorides the (110) and (103) peaks were used to calculate values of \( a \) and \( c \). From these unit-cell values the value of \( \sin \theta \) for the (101) peak was calculated. This calculated value was compared with the measured value and the percent discrepancy in \( \sin \theta \) was taken as the percent error in \( a \) and \( c \). The percentage errors in \( a \) and \( c \) for a number of determinations for fluorides of a given type were averaged to give an average percentage error which was assigned to all the \( a \) and \( c \) determinations of a given type, i.e., all untreated fluorides in a given mixed-fluoride system or all reacted fluorides in a given mixed-fluoride system.

For the orthorhombic fluorides the three best peaks in a given run were used to calculate values of \( a \), \( b \), and \( c \). Other peaks were used to estimate errors as described above. Pure \( \text{YF}_3 \) gave good data and the error assigned here was small. Other cerium-yttrium mixed fluorides were assigned the same higher percentage error in the determination of their unit-cell dimensions.
III. RESULTS AND DISCUSSION

A. Notation

In summarizing the results of the numerous fluorination runs on the various mixed fluoride systems it will be convenient to employ the following notation. Starting materials will be represented as Ce$_{0.8}$M$_{1-0.8}$F$_3$ or Tb$_{0.8}$M$_{1-0.8}$F$_3$, where $\delta$ represents the mole fraction of CeF$_3$ or TbF$_3$ in the mixed fluoride. In some cases the starting materials do not form a continuous range of solid solutions over the whole range of compositions. The solubility limits of starting materials as precipitated from solution at room temperature will be represented by $\delta'$ and $\delta''$ where $\delta'$ corresponds to the CeF$_3$ or TbF$_3$ mole fraction in a saturated solution of CeF$_3$ or TbF$_3$ in MF$_3$, and $\delta''$ corresponds to the CeF$_3$ or TbF$_3$ mole fraction in a saturated solution of MF$_3$ in CeF$_3$ or TbF$_3$. The products of fluorination do not form a continuous series of solid solutions. Here, the solubility limits correspond to a pressure of F$_2$ of 1 atmosphere and a temperature of 250°C. In this case $\alpha$ is the mole fraction of CeF$_4$ or TbF$_4$ in a saturated solution of tetrafluoride in MF$_3$, and $\beta$ is the mole fraction of cerium or terbium tetrafluoride in a saturated solution of MF$_3$ or MF$_4$ in tetrafluoride. In certain instances single phases can be produced in which only a portion of the CeF$_3$ or TbF$_3$ is oxidized. The mole fraction of oxidizable trifluoride not oxidized in such cases will be represented by $\gamma$ if the phase has an MF$_3$ structure or $\epsilon$ if the phase has a CeF$_4$ structure.

B. The CeF$_3$ - LaF$_3$ System

The results of fluorination runs on the CeF$_3$-LaF$_3$ system, which forms a continuous series of solid solutions, are presented in Fig. 5, in which the percentage of the total cerium oxidized to the +4 state is plotted against $\delta$. In this figure the solid curve represents complete reaction while the dotted curve represents the extent of reaction after
Fig. 5.

FLUORINATION OF THE Ce F₃-La F₃ SYSTEM

- Weight gain of pan contents in F₂.
- Helix balance deflections.
- Oxide formation determinations.

MU-14023
a 10- to 15-minute exposure to F₂ at about 250°C. The data show that the three methods used to determine the amount of cerium oxidized give reasonably close agreement in nearly all cases, and that there seems to be no systematic trend in any of the methods toward high or low values. It is possible to divide the range of compositions into three different regions corresponding to the nature of the reactions that occur. These regions correspond to δ > β, β > δ > α, and δ < α.

The results in the high cerium region (δ > β) indicate that the reaction appears to proceed in two steps. From Fig. 5 it can be seen that there are two separate curves in this region, indicating about 80% oxidation and complete oxidation of the cerium. The 80% oxidation corresponds to the initial step in the fluorination reaction and usually occurs rapidly (~10 min) as the sample is heated in F₂. Stable materials in which the cerium is ~80% oxidized can be obtained by cooling the samples after keeping them in F₂ at around 250°C for only about 15 minutes. These materials have the CeF₄ structure, and x-ray photographs reveal no lines corresponding to the LaF₃ structure. If the samples are kept in F₂ for a longer period (~70 hours) complete oxidation of the cerium occurs. The complete reaction appears to take about 2 to 3 hours at 250°C. Further heating beyond the 2- to 3-hour period results in no further weight gains.

It appears probable that the initial step, which involves a phase change, results in the oxidation of enough cerium to stabilize the monoclinic CeF₄ structure. Further oxidation is slower and involves the oxidation of +3 cerium present in the monoclinic structure. The two steps can be written as

\[
\begin{align*}
\text{Ce}_δ \text{La}_{1-δ} F_3 \, \text{F}_2 & = \text{Ce}^{IV} δ-ε \, \text{Ce}^{III} δ-ε \, \text{La}_{1-δ} F_3 \, 2 \beta-ε, \\
\text{(CeF}_4 \text{ structure)}
\end{align*}
\]

\[
\begin{align*}
\text{Ce}^{IV} δ-ε \, \text{Ce}^{III} ε \, \text{La}_{1-δ} F_3 + 2 \beta-ε & = \text{Ce}_δ \text{La}_{1-δ} F_3, \\
\text{(CeF}_4 \text{ structure)}
\end{align*}
\]
These reactions should occur at all values of \( \delta \) that are greater than \( \beta \). It has not been possible to fix the value of \( \beta \) accurately, since the value of \( \beta \) is indicated by the appearance of materials having the LaF\(_3\) structure in the fluorinated products and since the x-ray photographs of the completely fluorinated products in this region are of very poor quality. However, since the initial step of the above two reactions occurs down to \( \delta = 0.78 \), one can state \( 0.78 < \beta < 1.00 \).

In the intermediate cerium region (\( \beta > \delta > \alpha \)) the complete oxidation of cerium appears to take place rapidly (~ 15 min at ~ 250°C). There seems to be a slight further reaction if the procedure is continued for about 40 hours, as indicated by the high points on the solid line at \( \delta = 0.68 \). X-ray photographs clearly reveal the presence of two phases in the final products, one having the LaF\(_3\) and one having the CeF\(_4\) structure. As \( \delta \) decreases the LaF\(_3\) pattern becomes stronger and the CeF\(_4\) pattern becomes weaker.

The reaction that occurs in this region can be written as

\[
\text{Ce}_\delta \text{La}_{1-\delta} \text{F}_3 + \frac{5}{2} \ F_2 = \frac{\delta-\alpha}{\beta-\alpha} \text{Ce}_\beta \text{La}_{1-\beta} \text{F}_{3+\beta} + \frac{\beta-\delta}{\beta-\alpha} \text{Ce}_\alpha \text{La}_{1-\alpha} \text{F}_{3+\alpha}.
\]

The slight additional reaction, which probably involves the phase with the LaF\(_3\) structure, will be considered later. At the point \( \delta = \alpha \) the rate of the fluorination reaction appears to change. From this kinetic result the value of \( \alpha \) can be taken as being about 0.55. This large solubility of CeF\(_4\) in LaF\(_3\) is in agreement with the work of Schylter and Sillen\(^{29}\) on the coprecipitations of CeF\(_4\) with LaF\(_3\).

In the low cerium region (\( \delta < \alpha \)) the reaction is slower. About 20 hours are required for complete oxidation of the cerium. All the samples in this region were kept in \( \text{F}_2 \) for about 40 hours. Only one final phase having the LaF\(_3\) structure is produced. There appears to be an added weight gain over and above that required for complete oxidation of the cerium. This extra gain corresponds to about 0.1 of the weight gain required for complete cerium oxidation. No such weight gain was observed when pure LaF\(_3\) was treated with \( \text{F}_2 \).
Because the reaction in this region is slow it was possible to isolate substances in which partial cerium oxidation had occurred. These materials had a light tan color, in contrast to the white starting materials. The completely oxidized substances, which were allowed to react for 40 hours, had a light tan color, which became more intense as the amount of cerium present increased.

The reaction that occurs in this region can be written as

$$\text{Ce}_6\text{La}_{1-\delta}\text{F}_3 + \frac{5}{2} \text{F}_2 = \text{Ce}_6\text{La}_{1-\delta}\text{F}_{3+\delta} \tag{\text{LaF}_3 \text{ structure}}$$

The reason for the extra weight gains referred to above was more thoroughly investigated. If one excludes the possibility of oxidation of either La$^{3+}$ or Ce$^{4+}$ to higher valence states, there are two likely possibilities for this extra weight increase. If oxyfluorides or oxides were present in the starting materials, extra apparent weight gains would be observed upon exposure of these materials to fluorine. There is also the possibility that extra gas would be absorbed or adsorbed by the oxidized materials. Since the extra weight gain is always about 0.1 the weight gain calculated for cerium oxidation, the extra weight gain is roughly proportional to the number of defects introduced into the LaF$_3$ structure by cerium oxidation. Perhaps the tan color of the oxidized materials may also be related in some way to this extra weight gain. The gases that may be taken up by the fluorinated materials are atomic fluorine, HF, or F$_2$.

The oxyfluoride or oxide explanation can be eliminated as shown by the following considerations. Some of the starting materials were analyzed by converting the mixed trifluorides to oxides by heating to constant weight in air. Conversion of pure fluorides to oxides is quantitative, as shown by the work of Knudson. From the weight losses observed it was estimated that only about 1 to 2% of oxyfluoride could be present in these samples. Yet in order to produce the observed extra weight gains, amounts of oxyfluoride corresponding to about 30% of the total sample weight would have to be present. Also, these large quantities of oxyfluoride were not detected in x-ray photographs of the starting materials; the x-ray photographs showed only trifluoride lines.
Although the uptake of atomic fluorine would probably seem to be ruled out on energetic grounds, owing to the large dissociation energy of F₂, the fluorine atom is small enough in radius to fit into cation vacancies that might be present in the oxidized materials. Also the tan color found in these completely oxidized materials may be due to the presence of the unpaired electrons in atomic fluorine.

The presence of atomic fluorine can be confirmed or ruled out by measurements of the magnetic susceptibility of the oxidized materials. Take, for example, a 1-gram sample of an oxidized material containing 50 mole % LaF₃ and 50 mole % CeF₄, and containing a gram-atomic amount of atomic fluorine corresponding to 0.1 of the total molar amount of CeF₄ present. This is just the amount of atomic fluorine that might be taken up in the fluorination of a half-and-half mixture of CeF₃ and LaF₃. The 1-g sample contains ~1/2 g of CeF₄ or 0.0023 mole of CeF₄. In this sample, then, there should be present 0.00023 gram atom of atomic fluorine. Since atomic fluorine has the 2P³/₂ ground state and therefore a spin of 1/2, its magnetic moment as calculated from the simple "spin only" formula should be 1.73 Bohr magnetons. This value corresponds to a magnetic susceptibility of 1.3 x 10⁻³ cgs units per gram atom. The contribution to the magnetic susceptibility of the above material due to atomic fluorine should be about (1.3 x 10⁻³) (2.3 x 10⁻⁴) = 3.1 x 10⁻⁷ cgs units per gram of the above sample. This contribution must be added to the estimated diamagnetic susceptibility of the above sample for estimation the magnetic susceptibility of the sample when atomic fluorine is present.

Magnetic susceptibilities were measured on a Faraday-type magnetic susceptibility balance previously used to measure the susceptibilities of very small quantities of actinide compounds. The balance, which is schematically shown in Fig. 6, consisted of a vertical quartz torsion fibre to which a horizontal quartz balance beam was attached. A quartz sample holder could be rigidly suspended from one end of the beam and a tare weight could be suspended from the other end of the beam. By twisting the torsion fibre by means of a torsion wheel one could align the beam into such a position that two index fibres, one on each side of the
Fig. 6.
beam, were in line when observed by means of a comparison-microscope optical system. This position was taken as the reference position in the measurements. A permanent magnet could be moved close to or away from the sample by means of a mechanical system.

The procedure used in making susceptibility measurements was to determine the position of the torsion wheel at the reference position of the balance with the sample holder in position both when the magnet was away from the holder and close to the holder. Both positions of the magnet were reproducible. Thus the number of turns in the torsion wheel necessary to compensate for the action of the magnetic-field difference on the sample holder could be obtained by subtracting the torsion wheel reading of the "magnet out" position from the reading of the "magnet in" position. The sample holder was then filled with a known weight of Mohr's salt (ferrous ammonium sulfate) and the above operations were repeated. The effect of the magnetic field difference on sample holder plus Mohr's salt was thus obtained. By subtraction it was then possible to obtain the number of turns necessary to compensate for the Mohr's salt alone and thus calibrate the balance. This number of turns is directly proportional to the difference in force on the Mohr's salt produced by changing the magnet positions. The magnetic susceptibility of Mohr's salt was taken as $29.5 \times 10^{-6}$ cgs units/g at room temperature.

In measuring the susceptibility of the fluoride samples the same procedure was followed as with the Mohr's salt. Readings were taken on the empty sample holder and then on the sample holder containing a known weight of fluoride. The magnetic susceptibility of the sample was then calculated from the number of turns necessary to compensate for the sample, the weight of the sample, the number of turns necessary to compensate for the Mohr's salt, and the weight of the Mohr's salt. For example, in measuring the magnetic susceptibility of pure $\text{LaF}_3$, it was found that a $-3.11^\circ$ turn of the torsion wheel was required to compensate for a 0.79-mg sample of $\text{LaF}_3$, while a 0.1392-mg sample of Mohr's salt required a $100.3^\circ$ turn of the torsion wheel for compensation. Thus the magnetic susceptibility of $\text{LaF}_3$ is:
The susceptibility of pure LaF$_3$ was measured as described above and found to be $-(1.6 \pm 0.5) \times 10^{-7}$ cgs units/g. The susceptibility of a fluorinated sample containing 54.5 mole % CeF$_4$ and 45.5 mole % LaF$_3$, and which showed an extra 10% weight gain of fluorination, was found to be $-(1.5 \pm 0.2) \times 10^{-7}$ cgs units/g. The estimated errors in susceptibility were average errors calculated on the basis of variations in susceptibility-balance readings and errors in sample weighings. If the diamagnetic susceptibility of the fluorinated sample is taken as being the same as the diamagnetic susceptibility of LaF$_3$, it can be seen that no paramagnetism due to atomic fluorine was observed. On this basis it is possible to rule out the presence of atomic fluorine in the fluorinated samples.

If the extra weight gain of the fluorinated samples was due to the uptake of HF in the F$_2$ gas it might be possible that mixed cerium and lanthanum trifluorides would also take up extra HF, since these materials have the same structure though not the same number of lattice defects as do the fluorinated materials. In order to test this idea samples of LaF$_3$ and Ce$_{0.27}La_{0.73}$F$_3$ were heated in a nickel system with HF gas at 1 atmos pressure for 2.5 and 4 hours respectively at 150°C and allowed to cool in the presence of HF. In neither case did the samples show any gain in weight.

The cause of the extra weight gain has not been established. If the effect is real it seems probable that uptake of F$_2$, HF, or perhaps some other impurity in the F$_2$ gas may be responsible.

C. The CeF$_3$ - YF$_3$ System

The results of the fluorination of the CeF$_3$ - YF$_3$ system are presented in Fig. 7. In this system the starting materials do not form a continuous series of solid solutions, since CeF$_3$ and YF$_3$ have different structures. X-ray photographs of the strating materials were used to
FLUORINATION OF THE CeF₃-YF₃ SYSTEM

○ Weight gain of pan contents in F₂.
△ Helix balance deflections.
□ Oxide formation determinations.

Fig. 7.
set limits on the values of \( \delta' \) and \( \delta'' \). A careful examination of these photographs indicates that \( \delta' \) is probably in the range of 0.27 to 0.37 and that \( \delta'' \) probably falls in the range 0.57 to 0.67. X-ray photographs of fluorinated materials were used to set limits on the values of \( \alpha \) and \( \beta \). It was found that \( \beta \) probably falls in the range 0.27 to 0.37 and that \( \beta \) probably falls in the range 0.78 to 0.89.

Examination of Fig. 7 shows that complete oxidation of cerium occurs throughout the entire range of compositions. The fact that most of the points fall above the 100% value is probably explained by the fact that the fluorinated materials were observed to be slightly hygroscopic. Thus the sample weight would be somewhat high upon removal from \( \text{F}_2 \), due to moisture uptake. The rates of these reactions appear to be about the same throughout the whole composition range. Complete reaction occurred in from 2 to 5 hours at 250°C and in 1 atm. of \( \text{F}_2 \) for all the compositions plotted in Fig. 7. Further heating in \( \text{F}_2 \) resulted in no further reaction.

In writing equations for the various reactions that occur, it will be convenient to start with high values of \( \delta \) and work down to low \( \delta \) values. In the high-cerium-content region (\( \delta > \beta \)) only one final phase is produced, and the reaction is

\[
\text{Ce}_6 \gamma'_1 \delta \text{F}_3 + \frac{\delta}{2} \text{F}_2 = \text{Ce}_6 \gamma'_1 \delta \text{F}_{3+\delta}
\]

(\( \text{LaF}_3 \) structure) \( \text{CeF}_4 \) structure)

In the region for which we have \( \beta > \delta > \delta'' \), a single-phase starting material reacts to produce a two-phase product,

\[
\text{Ce}_6 \gamma'_1 \delta \text{F}_3 + \frac{\delta}{2} \text{F}_2 = \frac{\delta-\alpha}{\beta-\alpha} \text{Ce}_6 \gamma'_1 \beta \text{F}_{3+\beta} + \frac{\beta-\delta}{\beta-\alpha} \text{Ce}_6 \gamma'_1 \alpha \text{F}_{3+\alpha}
\]

(\( \text{LaF}_3 \) structure) \( \text{CeF}_4 \) structure) \( \text{YF}_3 \) structure)

At values of \( \delta \) less than \( \delta'' \), the situation becomes somewhat more complicated, since two possible reaction schemes are consistent with the experimental data. For \( \alpha < \delta' \) the reactions correspond to the first possibility; for \( \alpha > \delta' \) the reactions correspond to the second possibility.
The first possible reaction scheme will now be considered. In the region $\delta'' > \delta > \delta'$ two starting materials are present: $\text{Ce}_6'\text{Y}_1\delta''\text{F}_3'$, having the LaF$_3$ structure, and $\text{Ce}_6'\text{Y}_1\delta\text{F}_3'$, having the YF$_3$ structure. The following reactions occur in this region:

$$\text{Ce}_6'\text{Y}_1\delta''\text{F}_3' + \frac{\delta''}{2} \text{F}_2 = \frac{\delta'' - \alpha}{\beta - \alpha} \text{Ce}_{\beta'}\text{Y}_1\beta'\text{F}_{3+\beta} + \frac{\beta - \delta''}{\beta - \alpha} \text{Ce}_{\alpha'}\text{Y}_1\alpha'\text{F}_{3+\alpha}$$

(\text{LaF}_3\text{ structure}) \quad (\text{CeF}_4\text{ structure}) \quad (\text{YF}_3\text{ structure})

and

$$\text{Ce}_6'\text{Y}_1\delta\text{F}_3' + \frac{\delta}{2} \text{F}_2 = \frac{\delta - \alpha}{\beta - \alpha} \text{Ce}_{\beta'}\text{Y}_1\beta'\text{F}_{3+\beta} + \frac{\beta - \delta}{\beta - \alpha} \text{Ce}_{\alpha'}\text{Y}_1\alpha'\text{F}_{3+\alpha}$$

(\text{YF}_3\text{ structure}) \quad (\text{CeF}_4\text{ structure}) \quad (\text{YF}_3\text{ structure})

In the region $\delta' > \delta > \alpha$ the following reaction occurs:

$$\text{Ce}_6'\text{Y}_1\delta'\text{F}_3' + \frac{\delta}{2} \text{F}_2 = \frac{\delta - \alpha}{\beta - \alpha} \text{Ce}_{\beta'}\text{Y}_1\beta'\text{F}_{3+\beta} + \frac{\beta - \delta}{\beta - \alpha} \text{Ce}_{\alpha'}\text{Y}_1\alpha'\text{F}_{3+\alpha}$$

(\text{YF}_3\text{ structure}) \quad (\text{CeF}_4\text{ structure}) \quad (\text{YF}_3\text{ structure})

Finally, in the region $\delta < \alpha$, there is no formation of two phases on fluorination:

$$\text{Ce}_6'\text{Y}_1\delta\text{F}_3' + \frac{\delta}{2} \text{F}_2 = \text{Ce}_6'\text{Y}_1\delta'\text{F}_{3+\delta}$$

(\text{YF}_3\text{ structure}) \quad (\text{YF}_3\text{ structure})

The second possible reaction scheme results in some final phases that are not in equilibrium with each other. In the region $\delta'' > \delta > \alpha$ the two starting materials present are $\text{Ce}_6'\text{Y}_1\delta''\text{F}_3'$, having the LaF$_3$ structure, and $\text{Ce}_6'\text{Y}_1\delta\text{F}_3'$, having the YF$_3$ structure. These phases react as follows:

$$\text{Ce}_6'\text{Y}_1\delta''\text{F}_3' + \frac{\delta''}{2} \text{F}_2 = \frac{\delta'' - \alpha}{\beta - \alpha} \text{Ce}_{\beta'}\text{Y}_1\beta'\text{F}_{3+\beta} + \frac{\beta - \delta''}{\beta - \alpha} \text{Ce}_{\alpha'}\text{Y}_1\alpha'\text{F}_{3+\alpha}$$

(\text{LaF}_3\text{ structure}) \quad (\text{CeF}_4\text{ structure}) \quad (\text{YF}_3\text{ structure})

and

$$\text{Ce}_6'\text{Y}_1\delta\text{F}_3' + \frac{\delta}{2} \text{F}_2 = \text{Ce}_6'\text{Y}_1\delta'\text{F}_{3+\delta'}$$

(\text{YF}_3\text{ structure}) \quad (\text{YF}_3\text{ structure})
The phase Ce₅₃Ye₆F₁₃₊δ is not in equilibrium with the other two phases produced in this region and is unstable with respect to them. This is because the value of δ is such that after reaction occurs only saturated final solid solutions are thermodynamically stable. At the relatively low temperatures of these experiments, however, such thermodynamic equilibrium is probably not attained.

In the region α > δ > δ' the same two reactions occur. However, the two saturated phases are now unstable with respect to the phase Ce₅₃Ye₆F₁₃₊δ. Again, however, three distinct final phases are probably present owing to the lack of equilibrium attainment.

Finally, for δ < δ', only a single phase is produced as a product:

\[ Ce_{5.1-6}Y_{1-6}F_{3+δ} + \frac{δ}{2}F_2 = Ce_{5.1-6}Y_{1-6}F_{3+δ} \]

(YF₃ structure) (YF₃ structure)

D. The CeF₃ - PrF₃ System

From the results of the fluorination of the CeF₃-LaF₃ and CeF₃-YF₃ systems, it can be seen that the cerium is always completely oxidized to the +4 state. Therefore one would expect that in the CeF₃-PrF₃ system a similar complete oxidation of the cerium would occur. Since praseodymium also forms +4 ions the possibility existed that some of the praseodymium may also be oxidized even though pure PrF₃ cannot be oxidized with F₂. In particular it was thought that a solid solution of PrF₄ in CeF₄ might be more stable than a solid solution of PrF₃ in CeF₃. In such a case the increased Coulombic interaction energy of Pr⁺ with anion neighbors would overbalance the energy of ionization of Pr⁺⁺ to Pr⁺⁺⁺.

The results of the fluorination of the CeF₃-PrF₃ system are presented in Fig. 8. Since, from the value of δ and from the weight of starting material, it is possible to calculate the amounts of CeF₃ and
FLUORINATION OF THE CeF₃-PrF₃ SYSTEM

- Helix balance deflections.
- Weight gain of pan contents in F₂.

Fig. 8.
PrF$_3$ present, it becomes possible to calculate the weight gain for fluorine oxidation of the cerium and the weight gain for fluorine oxidation of the praseodymium. In all cases it was assumed that no oxidation of Pr$^{3+}$ occurred until all Ce$^{3+}$ had been oxidized.

Since the CeF$_3$-PrF$_3$ mixed trifluoride system forms a continuous series of solid solutions, the system can be compared to the CeF$_3$-LaF$_3$ system. It is again possible to divide the range of compositions into three regions corresponding to the reactions that occur. These regions are $\delta > \beta$, $\beta > \delta > \alpha$, and $\delta < \alpha$.

In the high-cerium region ($\delta > \beta$), 80% to 100% of the cerium is oxidized in about 15 min at 250$^\circ$C. A single phase having the CeF$_4$ structure is produced. Further heating in F$_2$ at 250$^\circ$C, even for as long as 10 days, causes no further reaction. By analogy with the CeF$_3$-LaF$_3$ system it seems probable that the reaction in this region is a two-step process, and that the second step, which involves oxidation of the praseodymium, is very slow at 250$^\circ$C. The results of fluorinations in the intermediate cerium region, which are given below, strongly imply that equilibrium is attained only after the praseodymium present has been oxidized. From the data the value of $\beta$ can be taken as falling in the range 0.88 to 0.93. The reactions that occur in this region can be written as

$$\text{Ce}_6\text{Pr}_{1-\delta}\text{F}_3 + \frac{\delta - \epsilon}{2} \text{F}_2 = \text{Ce}^{IV}_{\delta - \epsilon}\text{Ce}^{III}_{\epsilon}\text{Pr}^{III}_{1-\delta}\text{F}_{3+\delta-\epsilon}$$

(CeF$_4$ structure)

and

$$\text{Ce}^{IV}_{\delta - \epsilon}\text{Ce}^{III}_{\epsilon}\text{Pr}^{III}_{1-\delta}\text{F}_{3+\delta-\epsilon} + \frac{\epsilon - \delta + 1}{2} \text{F}_2 = \text{Ce}^{IV}_{\delta}\text{Pr}^{IV}_{1-\delta}\text{F}_4 \text{ (slow)}$$

(CeF$_4$ structure)

In the intermediate-cerium region ($\beta > \delta > \alpha$) two final phases are present. The fluorination data show a linear relationship between the percentage of total praseodymium oxidized and $\delta$. This linearity is simply explained by assuming that the praseodymium is oxidized in one of the final phases but not in the other. The reaction occurring in this region can be written as
In this region the reaction takes about 5 to 7 hours to go to completion.

The stabilization of PrF$_4$ in the CeF$_4$ lattice is a striking example of the phenomenon of valence inductivity.\textsuperscript{32} It has already been shown that, thermodynamically, it is quite possible for a fluoride, such as PrF$_3$, to be oxidized in a mixed crystal even though it cannot be oxidized when pure. Clearly the difficulty in oxidizing Pr$^{4+}$ to Pr$^{4+}$ is more than compensated for by the gain in stability of a crystal containing PrF$_4$ dissolved in CeF$_4$ over that of a crystal containing PrF$_3$ dissolved in CeF$_4$.

In the region of low cerium content ($\delta < \alpha$) the reaction results in the oxidation of only the cerium and in the formation of a single final solid phase. The value of $\alpha$ is close to 0.50, which is consistent with the value of $\alpha$ obtained in the CeF$_3$-LaF$_3$ system. The reactions in this region usually took about 5 to 7 hours to go to completion. The reaction observed is simply

$$\text{Ce}_8\text{Pr}_{1-8}\text{F}_3 + \frac{8}{2} (1-\alpha) + \alpha (\beta-1) \text{ F}_2 = \frac{8}{2} \alpha \text{ Ce}_8\text{Pr}_{1-8}\text{F}_{4} + \frac{8}{2} \beta \text{ Ce}_8\text{Pr}_{1-8}\text{F}_{4}$$

(CeF$_4$ structure)

$$+$$

$$\frac{\beta - \delta}{\beta - \alpha} \text{ Ce}_8\text{Pr}_{1-8}\text{F}_{3+\alpha}$$

(LaF$_3$ structure)

Weight gains somewhat greater than those corresponding to 100% cerium oxidation were observed here. The reason for such weight gains is probably the same as that in the case of the similar extra weight gains observed in the CeF$_3$-LaF$_3$ system.
E. The TbF₃ - LaF₃ System

It has already been mentioned that certain preliminary results indicated that oxidation of TbF₃ was hindered by the presence of rare earth impurities. It was also shown that the presence of such impurities could conceivably halt oxidation altogether. Thus it was shown that the free-energy change for the oxidation of TbF₃ in a mixed fluoride might be made positive if the value of ΔF for the reaction TbF₃ + 1/2 F₂ = TbF₄ was only slightly negative. In order to test this possibility of lack of terbium oxidation in mixed crystals, the reactions of the TbF₃ - LaF₃ and TbF₃ - YF₃ systems with F₂ gas were studied.

The results of the reactions of F₂ with TbF₃ - LaF₃ mixed fluorides are given in Fig. 9. It can be seen that there is a linear relationship between the percentage of total terbium oxidized and δ for δ > 0.65. For δ < 0.65 there appears to be an apparent 20% oxidation of the terbium present. In all cases the fluorides were heated to constant weight in F₂ at 250°C. In nearly every case the weight gains were observed over an ~ 40-hour period. Nearly all the samples were kept in F₂ for 80 to 130 hours.

X-ray results indicated YF₃-type and LaF₃-type phases for the starting materials in the region δ > 0.65. The fluorinated materials in this region gave very poor patterns, but CeF₄-type and LaF₃-type phases could be detected. In the region δ < 0.65 all fluorinated materials showed only the LaF₃ type phase.

These gravimetric and x-ray results allow one to write equations for the reactions occurring in this system. The value of δ' is about 0.65. The results would seem to indicate that the solubility of LaF₃ in TbF₃ is small (only at most a few mole %). For simplicity δ'' will be set equal to 1.0. Thus in the region δ > δ' two phases are present in the starting materials, TbF₃ and Tb₆La₁-δF₃. These two phases are present in the proportions (δ-δ'): (δ'-δ) respectively. If the Tb₆La₁-δF₃ phase is nonoxidizable, then the fraction of total terbium that is oxidized should be δ - δ'/δ' - δ'. This would result in the
Fig. 9.

FLUORINATION OF THE Tb F₃-LaF₃ SYSTEM

PERCENT TOTAL Tb OXIDIZED
linear relationship observed. Actually at \( \delta = \delta' \), an apparent 20% terbium oxidation is observed. This apparent oxidation is discussed below.

For \( \delta < \delta' \) only the phase \( \text{Tb}_\delta \text{La}_{1-\delta} \text{F}_3 \) is present. The results indicate that about 20% of the terbium in this phase is oxidized, i.e., \( (\delta - \gamma)/\delta \sim 0.2 \) in the equation

\[
\text{Tb}_\delta \text{La}_{1-\delta} \text{F}_3 + \frac{\delta - \gamma}{2} \text{F}_2 = \text{Tb}^{IV}_{\delta - \gamma} \text{La}^{III}_{1-\delta} \text{F}_{3+\delta - \gamma}
\]

(\( \text{LaF}_3 \) structure) (\( \text{LaF}_3 \) structure)

However, the weight gains corresponding to 20% oxidation of the terbium in this region amount to only \( \sim 0.1 \) to \( 0.2 \) mg. Several other factors might account for such small weight gains. The presence of small amounts of oxides in the starting materials, the uptake of small quantities of extra gas (as in the \( \text{CeF}_3 \)-\( \text{LaF}_3 \) and \( \text{CeF}_3 \)-\( \text{PrF}_3 \) systems), or slight attack of the nickel pans by \( \text{F}_2 \) could, singly or collectively, result in small weight gains. A possible way to settle the question of whether or not partial oxidation occurs would be to measure the magnetic susceptibility of such samples before and after treatment with \( \text{F}_2 \).

F. The \( \text{TbF}_3 - \text{YF}_3 \) System

The results of the reactions of \( \text{F}_2 \) with \( \text{TbF}_3 - \text{YF}_3 \) mixed fluorides are given in Fig. 10. Since \( \text{TbF}_3 \) and \( \text{YF}_3 \) form a continuous series of solid solutions over the whole range of compositions, it becomes possible to determine the amount of \( \text{YF}_3 \) that must be present in order to stop terbium oxidation. Examination of the results shows that at values of \( \delta \) above 0.93 to 0.94 terbium oxidation is complete, while at values of \( \delta \) below this figure there is only an apparent oxidation of about 10% of the terbium present. Complete oxidation of the terbium takes about 90 hours at 250°C. The completely oxidized samples were kept in \( \text{F}_2 \) for about 150 hours. All samples of unoxidized fluorides were kept in hot \( \text{F}_2 \) for about 110 hours. X-ray photographs on fluorinated samples showed
Fluorination of the TbF₃-YF₃ system

Fig. 10.
only YF$_3$ structure lines for the unoxidized materials and showed very poor patterns for the oxidized materials. These poor patterns probably correspond to poorly crystallized solids having the CeF$_4$ structure.

Evidently for $\delta > 0.93$ to 0.94 the reaction that occurs can be written as

$$\text{ThF}_3 + \frac{5}{2} F_2 = \text{Th}_5 Y_1 F_{13+6}$$

(CeF$_4$ structure)

Although the solubility of YF$_3$ in TbF$_4$ is unknown and may be small, the final product is written as a single phase. For $\delta < 0.93$ to 0.94 there seems to be no reaction and the 10% apparent oxidation can probably be explained by reasons similar to those given for the TbF$_3$-LaF$_3$ system. However, the possibility of true partial oxidation of the terbium cannot be ruled out. Careful magnetic-susceptibility measurements might settle this question.

One fact emerges from these studies on the terbium-containing mixed fluorides. When enough nonoxidizable fluoride is present the terbium is not completely oxidized. Thermodynamic arguments have been advanced that can explain such results. Of course, such results might also be explained by very slow reaction rates, which prevail when enough nonoxidizable fluoride is present. However, the analogous cerium-containing systems show complete oxidation over the whole range of compositions, and these systems very probably react by means of the same mechanism as is operative in the terbium-containing systems. In addition it is hard to explain the sudden cutoff of terbium oxidation in the TbF$_3$-YF$_3$ system by any sort of kinetic argument. If, however, the $\Delta F$ value for terbium oxidation becomes positive for values of $\delta < 0.93$ in this system, the cutoff is easily explained.

If the thermodynamic explanation is correct it becomes possible to estimate the $\Delta F^0$ value for the reaction $\text{ThF}_3 + \frac{1}{2} F_2 = \text{ThF}_4$. Consider the reaction occurring in the TbF$_3$-YF$_3$ system at $\delta = 0.935$ where $\Delta F = 0$. This reaction can be written in these steps:
\[ \text{Tb}_6\text{Y}_1\text{F}_3 = 6 \text{TbF}_3 + (1-6) \text{YF}_3, \]
\[ 8 \text{TbF}_3 + \frac{5}{2} \text{F}_2 = 8 \text{TbF}_4, \]
\[ 8 \text{TbF}_4 + (1-6) \text{YF}_3 = \text{Tb}_6\text{Y}_1\text{F}_3, \]

For \( \Delta F = 0 \), then \( -\Delta F_f = \Delta F_g + \Delta F_h \). Reference to Table I shows that \( \text{TbF}_3 \) and \( \text{YF}_3 \) form solutions that have a negative free energy of mixing, which is about 70% of the ideal value at room temperatures. At \( \delta = 0.935 \) the ideal free energy of unmixing is 250 cal. at 250\(^\circ\)C. This ideal value will be set equal to \( \Delta F_f \), and the 30% correction will be ignored. It can be seen that \( \Delta F_g \) is greater than \( -\Delta F_f \) and equal to \( -\Delta F_f - \Delta F_h \). However, since the value of \( \Delta F_h \) is unknown, one can only say that \( -\Delta F_f < \Delta F_g < 0 \).

Now, we have \( \Delta F^o = \Delta F_g / 0.935 \), so that a value of -250/0.935 or -278 cal. per mole \( \text{TbF}_3 \) can be set as the lower limit for \( \Delta F^o \), and 0 calories per mole \( \text{TbF}_3 \) can be set as the upper limit for \( \Delta F^o \). Since we have \( \Delta F^o = -RT \ln K \) and \( K = 1/(P_{F_2})^{1/2} \), the pressure of fluorine in equilibrium with \( \text{TbF}_3 \) and \( \text{TbF}_4 \) at 250\(^\circ\)C can be estimated as about 0.6 atmos. if \( \Delta F^o \) is given a value of -278 cal per mole of \( \text{TbF}_3 \). This result indicates that it might be possible to carry out an equilibrium study of the reaction \( \text{TbF}_3 + 1/2 \text{F}_2 = \text{TbF}_4 \) at comparatively low temperatures.

G. X-Ray Results

On the basis of x-ray work Schlyter and Sillen\(^{29}\) calculated the unit-cell dimensions of solid solutions of \( \text{CeF}_4 \) in \( \text{LaF}_3 \) formed by precipitation from solution. The unit-cell volumes of these materials were found to be somewhat less than unit-cell columns of solid solutions of \( \text{CeF}_3 \) and \( \text{LaF}_3 \) with the same lanthanum-cerium ratios. In the work presented here, unit-cell dimensions of solutions of \( \text{CeF}_4 \) in \( \text{LaF}_3 \) were also
measured, as were unit-cell dimensions of solid solutions of CeF$_3$ and LaF$_3$. These results, along with those of Schlyter and Siller, are given in Fig. 11, in which the unit-cell volumes of the hexagonal materials are plotted against $\theta$. It can be seen that the results of this investigation do not confirm those of the Swedish workers. One possible explanation for this discrepancy may be that the samples used by Schlyter and Sillen contained water, since they were produced by recrystallization from solution at 100°C, whereas the samples used in this investigation were undoubtedly dry.

Another possibility is that the extra weight gained on fluorination by the solutions of CeF$_4$ in LaF$_3$ may in some way be connected with the unit-cell value discrepancies.

An attempt was made to test this possibility by heating three samples of a solution containing 54.5 mole % CeF$_4$ and 45.5 mole % LaF$_3$, which had gained extra weight on fluorination, in high vacuum at 100°C, 200°C, and 300°C for 15-hour periods. Then the magnetic susceptibilities and unit-cell dimensions of these and related materials were measured. The following susceptibilities were obtained: fluorinated material not heated in vacuum,

$$x = -(1.5 \pm 0.2) \times 10^{-7} \text{ cgs units/g};$$

fluorinated material heated at 100°C,

$$x = -(0.67 \pm 0.09) \times 10^{-7} \text{ cgs units/g};$$

fluorinated material heated at 200°C,

$$x = (16.7 \pm 0.4) \times 10^{-7} \text{ cgs units/g};$$

fluorinated material heated at 300°C,

$$x = (22.7 \pm 0.5) \times 10^{-7} \text{ cgs units/g};$$

original nonfluorinated trifluoride solution with the same cerium-to-lanthanum ratio,

$$x = (120.0 \pm 0.5) \times 10^{-7} \text{ cgs units/g}.$$

If one assumes that the paramagnetic susceptibility is directly proportional to the amount of Ce$^{3+}$ ion present, the percentages of cerium oxidized in these samples are:

unheated material, 100% cerium oxidized;

100°C heated material, 99% cerium oxidized;
UNIT CELL VOLUMES IN THE Ce F₃-La F₃ SYSTEM

○ Untreated fluoride.
□ Completely fluorinated fluoride.
△ Schlyter and Sillen +3 Ce present.
▼ Schlyter and Sillen +4 Ce present.

Fig. 11.
200°C heated material, 85% cerium oxidized; 
300°C heated material, 80% cerium oxidized.
The unit-cell volumes of these heated samples did not differ significantly from the volume of the nonheated sample. If the extra gas gained on fluorination was driven off by heating, the effect did not show up in the unit-cell determinations. However, since the looked-for effect is small and the error in the unit-cell dimension measurements is relatively large, these results are not to be taken as conclusive. The best that can be said is that the cause of this discrepancy in unit-cell measurements is still not settled.

Some results of unit-cell measurements on orthorhombic materials in the CeF₃-YF₃ system are given in Fig. 12 along with the unit-cell volume of YF₃ as determined by Zalkin and Templeton. Although the error in the measurement on YF₃ is low, the errors become much greater in CeF₃-YF₃ or CeF₄-YF₃ mixtures. These mixtures are very poorly crystallized. Attempts to improve the quality of CeF₃-YF₃ mixed crystals by prolonged annealing at 1000°C in high vacuum followed by slow cooling were not successful in producing better crystals. It seems probable that the intrinsic distortion present in these crystals is responsible for the poor x-ray results. As can be seen from Fig. 12, no significant conclusions can be drawn from these measurements.

Results on unit-cell measurements in the CeF₃-PrF₃ system are given in Fig. 13. The patterns obtained here were slightly better than those obtained in the CeF₃-LaF₃ system. It can be seen that most of the points for the fluorinated materials fall below the curve for CeF₃-PrF₃ solid solutions. However, the effect is not large, and probably not so large as one would expect from the results of Schlyter and Sillen on the CeF₃-LaF₃ system. It is difficult to draw any further conclusions from these data.
UNIT CELL VOLUMES IN THE CeF$_3$-YF$_3$ SYSTEM

○ Untreated fluoride.
□ Completely fluorinated fluoride.
X Zalkin and Templeton.

MU-14030

Fig. 12.
UNIT CELL VOLUMES IN THE CeF₃-PrF₃ SYSTEM

- Untreated fluoride.
- Completely fluorinated fluoride.

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Fig. 13.
H. Density Measurements

When CeF₄ dissolves in LaF₃ or YF₃ or when LaF₃ or YF₃ dissolves in CeF₄, to form solid solutions, gross numbers of defects are introduced into the solvent lattice. In the first case these defects may be cation vacancies or interstitial anions. In the second case, the defects may be anion vacancies or interstitial cations. It was not possible to investigate the nature of the defects in the CeF₄ lattice, owing to the difficulty of getting accurate unit-cell dimensions from the poor x-ray data. However, since unit-cell dimensions were obtained for some of the defect solids having the LaF₃ structure, attempts were made to measure the densities of these materials in order to determine the nature of the defects present.

In order to account for the shrinkage in unit-cell size which they observed in solutions of CeF₄ in LaF₃, Schlyter and Sillen postulated that cation vacancies were present, since interstitial anions would undoubtedly cause a swelling of the unit cell. However, in view of the lack of confirmation of the results of Schlyter and Sillen observed in this investigation, some doubt exists as the presence of cation vacancies in these solutions. Interstitial fluoride ions have been observed as being the defects present in solid solutions of LaF₃ in SrF₂, YF₃ in CaF₂, and ThF₄ in CaF₂, so that the presence of the relatively small F⁻ ions in interstitial positions in the LaF₃ lattice probably cannot be ruled out on steric grounds.

If density measurements are combined with unit-cell dimensions it is possible to distinguish between the two types of defects. The following calculation illustrates the method. The LaF₃ structure has two La⁺³ ions and six F⁻ ions per unit cell. When defects are present let x = the number of La⁺³ ions per unit cell, y = the number of Ce⁺³ ions per unit cell, and z = the number of F⁻ ions per unit cell. Also consider a solid solution containing 50 mole % LaF₃ and 50 mole % CeF₄. The x-ray data of this investigation indicate that such a solution has a unit-cell volume of about 108 Å³.
For interstitial anions it can be seen that we have

\[
\begin{align*}
  x & = y, \\
  3x + \frac{1}{4}y & = z, \\
  x + y & = 2.
\end{align*}
\]

The solutions of these equations are \(x = 1, y = 1, z = 7\). The density of this material is then

\[
\frac{\text{Ce} + \text{La} + \text{TF}}{(108 \times 10^{-24}) (6.02 \times 10^{23})},
\]

or 6.36, where the chemical symbols represent atomic weights. For cation vacancies it can be seen that we have

\[
\begin{align*}
  x & = y, \\
  3x + \frac{1}{4}y & = z, \\
  z & = 6.
\end{align*}
\]

The solutions of these equations are \(x = 6/7, y = 6/7, \) and \(z = 6\), and the calculated density is 5.60. An experimental determination of the density of this material should settle the question as to the type of defects present.

Densities were determined pycnometrically, with toluene as the displacement liquid. Special pycnometers having a volume of about 15 ml and equipped with standard-taper glass stoppers having 1/2 mm capillaries were used. The pycnometers also had glass caps, which prevented evaporation. The toluene used was Baker and Adamson reagent grade, which has a maximum boiling range of 1.0°C. The toluene was dried over sodium and refluxed to drive off dissolved gases before being used in density measurements. In order to test the reliability of the measurements the densities of liquid mercury and solid powdered \(\text{CeO}_2\), for which the unit-cell dimension was 5.411 Å were measured. The x-ray density of this \(\text{CeO}_2\) is 7.216.

The pycnometers were first weighed empty, then filled with water at 25.00 ± 0.01°C and weighed, then filled with toluene at 25.00 ± 0.01°C and weighed. The density of toluene was calculated from these measurements and was taken as 0.8609 at 25.00°C.
In the mercury density determinations, the pycnometers were weighed empty, then filled with toluene at 24.97 ± 0.01°C and weighed, then weighed containing ~ 0.06 ml of mercury, and then weighed containing the mercury and filled with toluene at 24.97 ± 0.01°C. The average density of the mercury was calculated from two separate determinations as 13.48. The true density of mercury at 25°C is 13.53. The small volumes of mercury taken approximately corresponded to the volume of CeO₂ used in the CeO₂ density determinations. It can be seen that the results are within 1/2% of the correct value.

Although this method gave satisfactory results with mercury, such was not the case with CeO₂. Repeated attempts to obtain density measurements in agreement with the x-ray density of pure CeO₂ failed. In the final CeO₂ determinations the same procedure was followed as in the mercury determinations, with the exception that after some of the toluene was added to the weighed sample of CeO₂, the slurry was boiled for at least 1/2 hour with constant stirring in order to remove air from its CeO₂. Two determinations using this method gave values of 6.898 and 6.895 for the density of CeO₂. These results, which are more than 4% too low, probably indicate that the CeO₂ crystals contain occluded air that cannot be removed by boiling. However, the possibility that these crystals might contain large numbers of Schottky defects cannot be ruled out.

In view of the fact that the mixed fluorides form much poorer crystals than CeO₂ does and that both the fluorides and CeO₂ are finely powdered materials, attempts to measure the densities of the mixed fluorides were abandoned. It seems likely that large crystals, such as those obtained from melts, would be necessary for accurate density determinations. Accurate density determinations of mixed fluorides have been obtained from cooled melts. However, there is no easy way of obtaining such crystals of solutions of CeF₄ in LaF₃. The question of the defects present in such solutions remains unanswered.
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