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If the incidence rates as reported by Walton are in error slight differences appear. For  $\gamma = 1140$ , incidence rates of 1.0, 2.33, and  $7.0 \times 10^{13}$  atoms/cm<sup>2</sup>/sec give the result  $\Delta G_{des} - \Delta G_{sd} = 0.36$  eV and  $\gamma^3 f(\theta) = 1.32 \times 10^9$ for all points considered together. As shown in Fig. 2, the points lie within the scatter band of the "correct" data. The Pound plot is more sensitive to changes in incidence rate than in  $\gamma$ .

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## Mass Spectrometry at High Temperatures. XVIII. The Stabilities of the Mono- and Difluorides of Scandium and Yttrium

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Mono-, di-, and trifluorides of Sc and Y have been identified in the vapors over mixtures of the corresponding metals and CaF2 in Ta-Knudsen cells at high temperatures. Equilibria among these molecules and Ca and CaF have been studied by a mass spectrometer and their dissociation energies have been determined.

## INTRODUCTION

The monofluorides of Sc and Y have been detected, their optical spectra studied, and the nature of the bonding considered by several authors.<sup>1-3</sup> Attempts have been made to calculate their dissociation energies from a Birge-Spooner extrapolation of the spectroscopic data, but the results obtained vary as much as 1.5 eV, indicating that the available spectroscopic data are not complete enough to permit reliable calculations of the dissociation energies of ScF and YF. An alternative method, used previously in the mass spectrometric studies of gaseous equilibria among the subfluorides of the rare-earth metals<sup>4</sup> has allowed a quantitative determination of the stabilities of these molecules. There have been no previous experimental studies of the gaseous difluorides.

The present paper reports a mass-spectrometric determination of the stabilities of scandium and yttrium mono- and difluorides.

## EXPERIMENTAL PROCEDURE AND RESULTS

The detailed description of the experimental apparatus and procedures are given elsewhere.4,5

The subfluorides of Sc and Y were obtained by heating these metals with CaF2 in a Ta-Knudsen cell. The

TABLE I. Appearance potentials and neutral precursors of ions in the Sc-Ca-F and Y-Ca-F systems.

Ion	Appearance potential (eV)	Neutral precursor	
Ca <sup>+</sup>	6.0	Ca	
$CaF^+$	6.5	CaF	
$Sc^+$	6.5	Sc	
$ScF^+$	6.3	ScF	
$\mathrm{ScF}_2^+$	7.0	$\mathrm{ScF}_2$	
	13.5	$ScF_3$	
$Y^+$	16.5	5	
$YF^+$	7.5	$\mathbf{YF}$	
${ m YF_{2}^{+}}$	7.0	$YF_2$	
	14.0	$YF_3$	

ionization-efficiency curves of the important ions observed are shown in Figs. 1 and 2, and the values of the appearance potentials are listed in Table I.

#### The Sc-Ca-F System

As one can see from the figures, the ionization efficiency curves establish the presence of Ca and Sc

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Number	Av temp (°K)	Reaction	$\Delta H_{\mathbf{T}}^{\circ}$ (kcal mole <sup>-1</sup> )	$\frac{\Delta H_{298}^{\circ}}{(\text{kcal mole}^{-1})}$
(a)	1410	CaF(g)+Sc(g)=Ca(g)+ScF(g)	-15.8±1.2	$-15.8\pm2$
(b)	1410	$2CaF(g)+Sc(g)=2Ca(g)+ScF_2(g)$	$-28.9{\pm}2.6$	$-31.1 \pm 3$
(c)	1410	$3CaF(g) + Sc(g) = 3Ca(g) + ScF_3(g)$	$-60.3 \pm 1.7$	$-63.1\pm 2$

TABLE II. Heats of reactions in the Sc-Ca-F system.



FIG. 3. Second-law plots for data on Sc-Ca-F system.

atoms, as well as CaF, and the mono-, di-, and trifluoride species for Sc and Y in the gas phase. The appearance potential curve for the  $Y^+$  ion starts at 16.5 eV. This value is much higher than the ionization potential of Y, indicating no detectable amounts of Y atoms in the effusing vapors in the temperature range investigated. The ion currents were measured at different temperatures by using low-energy electrons, about 5 eV above the appearance potentials. The MF<sub>3</sub>-pressures were obtained from measurements of the total MF<sub>2</sub><sup>+</sup> ion intensities at 18 eV with correction for the formation of MF<sub>2</sub><sup>+</sup> from MF<sub>2</sub> by direct ionization. The ion intensities were used to calculate the ion current analogs of the equilibrium constants for the fluorineexchange reactions. The reaction enthalpies were derived from the plots of log $K_i$  vs 1/T, by the second-law procedure.

In Ca-Sc-F systems, three simple fluorine-exchange reactions of the type

$$nCaF(g) + Sc(g) = nCa(g) + ScF_n(g)$$
 (n=1, 2, 3)  
(1)

were considered. The heats of dissociation of scandium fluorides,  $\Delta H_{\text{stoms}}^{\circ}(\text{ScF}_n)$  were derived from the reaction enthalpies  $\Delta H_n$  and the known dissociation energy of CaF, 125.0 $\pm 2$  kcal mole<sup>-15</sup>:

$$\Delta H_{\text{atoms}}^{\circ}(\text{ScF}_{n}) = -\Delta H_{n,298} + nD_{298}^{\circ}(\text{CaF}). \quad (2)$$

The second-law plots of the reactions in the Ca-Sc-F system are presented in Fig. 3, and the reaction enthalpies listed in Table II.

From the values of  $\Delta H_n$ ,  $D_{298}^{\circ}(\text{CaF})$  and by employing the reaction (2), one obtains the dissociation energies of scandium fluorides:

$$D_{298}^{\circ}(ScF) = 140.8 \pm 3.2 \text{ kcal/mole}^{-1}$$

$$\Delta H_{\text{atoms}} \circ [\text{ScF}_2(g)] = 281.1 \pm 6 \text{ kcal/mole}^{-1},$$

$$\Delta H_{\text{atoms}} \circ [\text{ScF}_3(g)] = 438.1 \pm 6 \text{ kcal/mole}^{-1}.$$

## Y-Ca-F System

The lack of clear evidence for the existence of Y(g) species in the effusing vapors over  $Y-CaF_2$  mixture made impossible a determination of the dissociation

Number	Av temp (°K)	Reaction	$\Delta H_T^{\circ}$ (kcal mole <sup>-1</sup> )	$\Delta H_{298}^{\circ}$ (kcal mole <sup>-1</sup> )
 (d)	1337	$YF(g)+2CaF(g)=YF_{a}(g)+2Ca(g)$	$-57.3 \pm 3.0$	$-59.7\pm5.0$
(e)	1337	$YF_2(g)$ +CaF(g) = $YF_3(g)$ +CaF(g)	$-38.5\pm3.0$	$-41.3\pm5.0$

TABLE III. Heats of reactions in the Y-Ca-F system.

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energies of yttrium fluorides from direct exchange reactions of the type (1). As an alternative, use was made of data from fluorine bomb calorimetry which establish  $\Delta H_f [YF_3(s)] = -410.7 \pm 0.4 \text{ kcal/mole}^{-1.6}$  and of equilibria which do not include yttrium atoms as reactants. The reactions studied and their enthalpies are given in Table III. The second-law plots of the equilibrium constants are shown in Fig. 4.

TABLE IV. Bond strengths of Sc and Y fluorides.

м	D(M-F)	D(FM-F) (in kcal mole <sup>-1</sup> )	$D(\mathbf{F}_{2}\mathbf{M}-\mathbf{F})$
Sc	140.8±3	140.3±5	157±7
Y	143.6±5	143.4±7	$166 \pm 10$

<sup>6</sup> E. Rudzitis, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 69, 2305 (1965).

From the measured heat of Reaction (d) (Table III) and available data for  $D_{298}^{\circ}(CaF)$ ,  $^{5}\Delta H_{f}^{\circ}(YF_{3})$ ,  $^{6}\Delta H_{s}^{\circ}(YF_{3})$ ,  $^{7}\Delta H_{s}(Y)$ ,  $^{8}$  and  $D_{298}^{\circ}(F_{2})$ ,  $^{9}$  one obtains the dissociation energy of YF,  $D_{298}^{\circ}(YF) = 143.6 \pm 5$  kcal mole<sup>-1</sup> ( $6.2 \pm 0.2$  eV). The same procedure applied to Reaction (e), gives the atomization energy of YF<sub>2</sub>,  $\Delta H_{stm}^{\circ}[YF_{2}(g)] = 287.0 \pm 7.0$  kcal mole<sup>-1</sup>.

Table IV lists the bond strengths of scandium and yttrium fluorides.

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