

$\text{BCl}_4^-$ . Instrumental characteristics make difficult the assessment of the intensity of the absorption at  $377\text{ cm}^{-1}$  but, if it is weak as has been assumed, it could be the symmetric B-Cl stretching frequency,  $\nu_1$ , of  $\text{BCl}_4^-$ . This is an infrared-forbidden band in the isolated species of  $T_d$  symmetry but may become weakly allowed owing to crystal perturbations. This effect has been proposed in the interpretation of the infrared spectrum of potassium tetrafluoroborate.<sup>22</sup>

The increases in Se-X absorption frequencies attending adduct formation would not be expected if the adducts were represented by structural formulation III. For a halogen-bridged structure little change in the disposition of groups about the selenium atom would be required, and fundamental frequency shifts would be unexpected, except possibly for the Se-X bridging bond. Viewing this bridging as the coupling of two oscillators for which the force constant  $k_{\text{Se-X}}$  is less than  $k_{\text{B-X}}$ , a decrease in the value of  $k_{\text{Se-X}}$  would be expected when the coupling occurs. This should result in a decrease in the absorption frequency of the bridging Se-X group.

A final point of interest in the infrared data presented in Table I is the apparently enhanced intensities of Se-C stretching frequencies of the dimethylselenium dihalide adducts as compared to the dimethylselenium dihalides themselves. Since band intensity depends upon the change in electric dipole moment with stretching motion along the bond axis, an intensity increase is in accord with the formation of a charged species, the  $[\text{SeX}(\text{CH}_3)_2]^+$  cation.

(22) N. N. Greenwood, *J. Chem. Soc.*, 3811 (1959).

The infrared evidence provided here is thus best interpreted in favor of the ionic formulations II for these adducts.

## Conclusions

While it might be argued that the presence of two electron-releasing groups, *e.g.*, methyls, in a four-coordinated molecule having selenium (or sulfur or tellurium) as the central atom should result in the enhancement of the bond-forming capacity of the unshared electron pair, it develops in the present case that the rupture of an Se-X bond and transfer of a halide ion is the preferred reaction route, as it is with the tetrahalide molecules. That classical Lewis basicity for those molecules in which the central atom possesses five electron pairs, one of which is stereochemically active but not involved in bond formation, has not yet been reported is perhaps not surprising, since the attachment of two chlorine atoms to the selenium atom in the  $(\text{CH}_3)_2\text{Se} \cdot \text{BCl}_3$  adduct would work against the formation and maintenance of a stable Se-B bond through both the steric and electron-withdrawing effects of the added atoms. Other related systems are under investigation and will be reported upon in due course.

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# Mass Spectrometric Studies at High Temperatures. VIII. The Sublimation Pressure of Iron(II) Fluoride

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*Mass spectrometric studies of  $\text{FeF}_2$  sublimation from a Knudsen cell have established  $\text{FeF}_2(\text{g})$  as the vapor species and  $\Delta H^\circ_{298}(\text{sublimation}) = 75.6 \pm 1.0\text{ kcal. mole}^{-1}$ .*

## I. Introduction

It has been pointed out in previous papers in this series<sup>1,2</sup> that, in general, reliable Knudsen or Langmuir vaporization or sublimation rates for the transition metal fluorides have not been available. Because of this, the review of Brewer, Somayajulu, and Brackett<sup>3</sup> on the thermodynamic properties of the gaseous metal dihalides includes many estimated heats of sublimation. In this work, the sublimation rate of  $\text{FeF}_2$  has been

(1) R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.*, **86**, 5090 (1964).

(2) T. C. Ehlert, R. A. Kent, and J. L. Margrave, *ibid.*, **86**, 5093 (1964).

(3) L. Brewer, G. R. Somayajulu, and E. Brackett, *Chem. Rev.*, **63**, 111 (1963).

measured and the vapor species identified by the Knudsen technique employing a mass spectrometer.

## II. Experimental Section

The mass spectrometer employed in this work has been described previously.<sup>4</sup> Temperatures below  $800^\circ$  were measured with a Ray-Tek R-7S infrared pyrometer equipped with a lead sulfide detector and an achromatic lens. This instrument operates in the spectral region from  $1.8$  to  $2.5\ \mu$  and can be focused on a 1-mm. black body hole from a distance of 15 in. Both the infrared and optical pyrometers were used to measure temperatures in the range  $800$  to  $900^\circ$ , and for all temperatures the measurements differed by no more than  $\pm 3^\circ$ .

The  $\text{FeF}_2$  powder was obtained from the Ozark-Mahoning Co. of Tulsa, Okla., and the only impurity

(4) G. D. Blue, J. W. Green, R. G. Bautista, and J. L. Margrave, *J. Phys. Chem.*, **67**, 877 (1963).

noted in the mass spectrum was water. All samples were extensively degassed in the instrument before temperature-dependence studies were initiated.

### III. Sublimation Study of FeF<sub>2</sub>

The sublimation rate was measured and the vapor species identified between 965 and 1149°K. by means of the mass spectrometric technique. Ionic species formed by electron bombardment of the effusate from the tantalum Knudsen cell were Fe<sup>+</sup>, FeF<sup>+</sup>, FeF<sub>2</sub><sup>+</sup>, and small amounts of TaF<sub>4</sub><sup>+</sup>, TaF<sub>3</sub><sup>+</sup>, TaF<sub>2</sub><sup>+</sup>, TaF<sup>+</sup>, and Ta<sup>+</sup>. The TaF<sub>n</sub><sup>+</sup> species are believed to be due to dissociative ionization of TaF<sub>3</sub>(g). No dimers or higher polymers of FeF<sub>2</sub>(g) were observed although the spectrum was scanned to mass 400. The relative isotopic abundances of the various Fe species were checked and found to agree with the values in the literature.

Ionization efficiency curves for the observed ions at 1130°K. are shown in Figure 1. In each case the measured ion intensity was corrected for background and photoionization effects.<sup>5</sup> Using as a standard the known value<sup>6</sup> of 10.4 e.v. for the ionization potential for mercury, one obtains appearance potentials for FeF<sub>2</sub><sup>+</sup>, FeF<sup>+</sup>, and Fe<sup>+</sup> equal to 11.3, 12.6, and 16.5 e.v., respectively, with estimated uncertainties of ±0.3 e.v. The appearance potentials and the shapes of the ionization efficiency curves for FeF<sup>+</sup> and Fe<sup>+</sup> indicate that these ions result from the dissociative ionization of FeF<sub>2</sub>(g) rather than from simple ionization of the gaseous species FeF and Fe.

Two independent methods were used to determine the heat of sublimation of FeF<sub>2</sub> from the experimentally observed FeF<sub>2</sub><sup>+</sup> ion currents. The intensity of the <sup>56</sup>FeF<sub>2</sub><sup>+</sup> peak, using 75-v. electrons, was followed as a function of temperature. By making use of the ion current-pressure relationship<sup>7</sup>  $p = kI^+T$  and the integrated form of the Clausius-Clapeyron equation, a value of ΔH<sub>T</sub> which is independent of the proportionality constant,  $k$ , may be obtained. Plotting log ( $I^+T$ ) vs.  $1/T$  yields a heat of sublimation of  $72.4 \pm 1.2$  kcal. mole<sup>-1</sup>, where the uncertainty quoted is the standard deviation of the least-squares treatment. The true uncertainty might be as much as two or three times this figure depending on the actual temperature gradients in the crucible. Because no heat capacity data for FeF<sub>2</sub>(s) were available, the heat capacity for FeF<sub>2</sub>(s) was estimated from a combination of the data for MnF<sub>2</sub>(s) listed by Mah<sup>8</sup> and the data for Mn(s) and Fe(s) presented by Stull and Sinke.<sup>9</sup> Thermodynamic functions for FeF<sub>2</sub>(g) were calculated from the parameters presented by Brewer and co-workers.<sup>3</sup> When corrected to 298°K., the second-law heat of sublimation becomes  $\Delta H_{298}^\circ = 75.3 \pm 1.2$  kcal. mole<sup>-1</sup>.

An alternative approach is to calculate  $\Delta H_{298}^\circ$  for each temperature from the absolute pressure and the

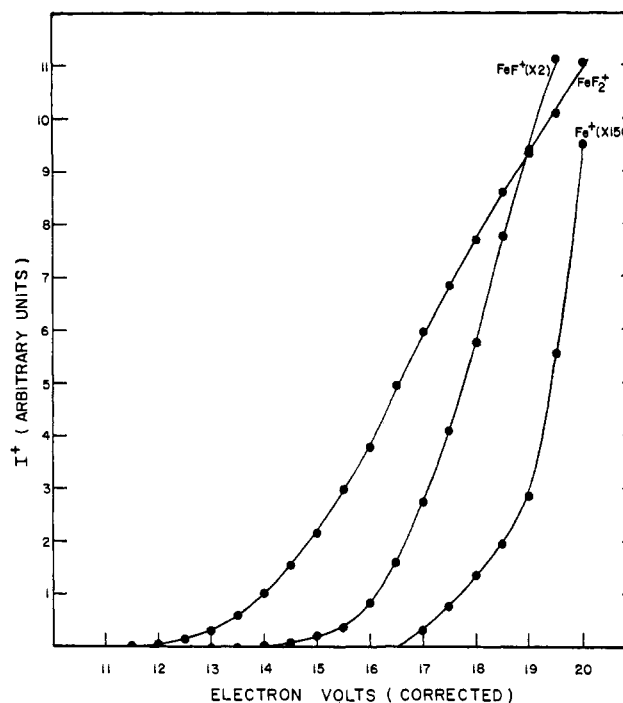


Figure 1. Ionization efficiency curves for species observed over FeF<sub>2</sub> at 1130°K.

free-energy function change ( $\Delta f_{ef}$ ) for the reaction. In order to determine the instrument constant,  $k$ , a weighed sample of previously degassed FeF<sub>2</sub> was vaporized from the crucible at a constant temperature, and the intensity of the <sup>56</sup>FeF<sub>2</sub><sup>+</sup> peak was followed as a function of time. At 1076°K.,  $9.08 \times 10^{-3}$  g. effused in 150 min. through an orifice  $1.54 \times 10^{-2}$  cm.<sup>2</sup> in area. By use of the Knudsen equation, the pressure was calculated to be  $5.0 \times 10^{-6}$  atm. The value of  $k$ , determined to be  $1.5 \times 10^{-12}$ , was combined with the least-squares equation for log ( $I^+T$ ) as a function of reciprocal temperature to yield the vapor pressure equation

$$\log P (\text{atm.}) = \frac{-(1.582 \pm 0.026)10^4}{T (^\circ\text{K.})} + 9.42 \pm 0.24$$

The value of  $k$  was also used to calculate a value of log  $P$  for each observation. The values of log  $P$  were then combined with the free-energy functions for FeF<sub>2</sub>(s) and FeF<sub>2</sub>(g) taken from Brewer, *et al.*,<sup>3</sup> to obtain a third-law heat of sublimation. The results of the mass spectrometric runs are presented in Table I and plotted in Figure 2.

While the small standard deviation in the third-law heat reflects the reproducibility of the measurements, the true uncertainty must reflect possible errors in the estimated thermodynamic functions; hence, the third-law heat is taken as  $75.6 \pm 1.0$  kcal. mole<sup>-1</sup>. The major inherent errors in the second-law results are those in temperature measurement. In practice, uncertainties of ±3 kcal. mole<sup>-1</sup> are usual in the temperature range covered by this investigation, and the second-law heat of sublimation is taken to be  $75.3 \pm 3.0$  kcal. mole<sup>-1</sup>.

When the heat of sublimation of FeF<sub>2</sub> is combined with the heat of formation of FeF<sub>2</sub> cited by Brewer, *et al.*,<sup>3</sup> the heat of sublimation of iron,<sup>9</sup> and the dis-

(5) W. A. Chupka and M. G. Inghram, *J. Phys. Chem.*, **59**, 100 (1955).

(6) C. E. Moore, National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1949.

(7) W. A. Chupka and M. G. Inghram, *J. Chem. Phys.*, **21**, 371 (1953).

(8) A. D. Mah, U. S. Department of Interior, Bureau of Mines, Report of Investigations, No. 5600, Mines Bureau, Pittsburgh, Pa., 1960.

(9) D. R. Stull and G. C. Sinke, *Advances in Chemistry Series*, No. 18, American Chemical Society, Washington, D. C., 1956.

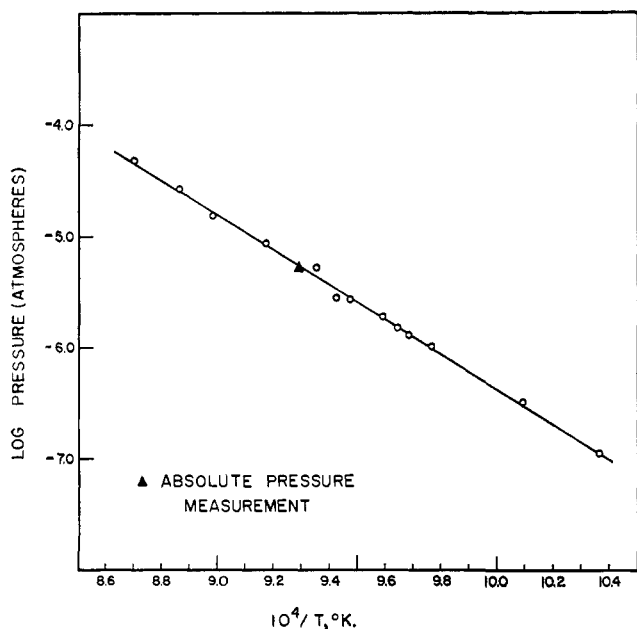
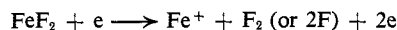


Figure 2. Vapor pressure data for  $\text{FeF}_2$ .

sociation energy of fluorine,<sup>10</sup> one calculates the atomization energy for  $\text{FeF}_2(\text{g})$  as  $230 \pm 10 \text{ kcal. mole}^{-1}$ , with much of the uncertainty caused by the lack of reliable measurements of the heat of formation of solid  $\text{FeF}_2$ .<sup>11</sup> Since the  $\text{Fe}^+$  ion is presumably formed by one of the processes indicated



one can calculate an atomization energy from the appearance potential ( $16.5 \pm 0.3$ ) and the ionization potential of  $\text{Fe}$ .<sup>8</sup> Thus, assuming  $\text{F}_2$  molecules as products

$$AP(\text{Fe}^+/\text{FeF}_2) \geq \Delta H_{\text{atom}} + IP(\text{Fe}) - D(\text{F}_2)$$

$$\Delta H_{\text{atom}} \leq 10.2 \pm 0.5 \text{ e.v. or } 235 \pm 10 \text{ kcal. mole}^{-1}$$

This is in agreement with the calculated heat and seems to preclude F atoms or negative ions as significant products in the fragmentation. The average Fe-F bond strength is  $115 \pm 5 \text{ kcal. mole}^{-1}$  (5.0 e.v.) and the standard heat of formation of  $\text{FeF}_2(\text{g})$  at  $290^\circ\text{K.}$  is  $-92.5 \pm 5 \text{ kcal. mole}^{-1}$ .

(10) J. G. Stamper and R. F. Barrow, *Trans. Faraday Soc.*, **54**, 1592 (1958).

(11) See original data cited in National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

Table I. Mass Spectrometric Data for  $\text{FeF}_2$  Sublimation

Temp., °K.	$I(\text{FeF}_2^+)$ , arbitrary units	$-\text{Log } P$ , atm.	$-\Delta f_{ef}$ , cal. deg. <sup>-1</sup> mole <sup>-1</sup>	$\Delta H_{298}^\circ$ , kcal. mole <sup>-1</sup>
1149	267.0	4.330	45.68	75.25
1129	155.0	4.577	45.78	75.33
1114	89.0	4.824	45.85	75.66
1091	51.3	5.072	45.97	75.48
1070	26.5	5.277	46.06	75.12
1055	16.6	5.577	46.14	75.60
1043	11.9	5.726	46.20	75.51
1033	7.80	5.914	46.24	75.72
1025	6.27	6.012	46.28	75.63
1091	50.1	5.082	45.97	75.53
1062	17.1	5.561	46.10	75.99
1037	8.28	5.886	46.22	75.86
991	2.04	6.514	46.42	75.54
965	0.73	6.972	46.48	75.64
1076 <sup>a</sup>	31.4	5.301	46.04	75.64
				Average = $75.56 \pm 0.23$

<sup>a</sup> Absolute pressure measurement, corrected for change in multiplier gain.

Two attempts were made to produce experimentally  $\text{FeF}(\text{g})$  in the Knudsen cell and to determine its dissociation energy. In the first attempt, about 200 mg. of iron wire was added to the  $\text{FeF}_2$  in the Knudsen cell in order to produce the equilibrium  $\text{Fe}(\text{g}) + \text{FeF}_2(\text{g}) = 2\text{FeF}(\text{g})$ . Because of the large difference in the heats of sublimation of  $\text{Fe}^0$  and  $\text{FeF}_2$ , it was impossible to produce sufficient  $\text{Fe}(\text{g})$  to follow conveniently equilibrium reaction. In a second attempt, iron wire was heated with  $\text{CaF}_2$  to produce the equilibrium  $\text{CaF}_2(\text{g}) + \text{Fe}(\text{g}) = \text{CaF}(\text{g}) + \text{FeF}(\text{g})$ . However,  $\text{Fe}^+$  was the only iron-containing species observed in the spectrum. The value of  $D_{298}^\circ(\text{CaF})$  has been determined to be 5.44 e.v.<sup>4</sup> Because the heats of sublimation of  $\text{Fe}$  and  $\text{CaF}_2$  differ by less than 5 kcal. mole<sup>-1</sup><sup>4,9</sup> and because the sensitivity of the mass spectrometer is such that the ion intensity of a species whose partial pressure is 0.1% of the total pressure can be measured easily, one can only conclude that the dissociation energy of  $\text{FeF}(\text{g})$  is less than 5.0 e.v.

If the ratio  $D(\text{MF})/\Delta H_a(\text{MF}_2) = 0.46 \pm 0.03$ , as has been found for the alkaline earth fluorides<sup>4</sup> and other transition metal fluorides,<sup>1</sup> then the predicted value for  $D(\text{FeF})$  becomes  $106 \pm 6 \text{ kcal. mole}^{-1}$  ( $4.6 \pm 0.3 \text{ e.v.}$ ), in good agreement with calculations based on an ionic model.

*Acknowledgments.* This work has been supported by the United States Atomic Energy Commission.