[Contribution from the Department of Chemistry, Rice University, Houston, Texas]

Mass Spectrometric Studies at High Temperatures. V. The Sublimation Pressure of Manganese(II) Fluoride and the Dissociation Energy of Manganese(I) Fluoride

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Received June 19, 1964

Mass spectrometric studies of MnF_2 sublimation and evaporation from a Knudsen cell have established $MnF_2(g)$ as the major vapor species and $\Delta H°_{298}$ [sublimation] = 76.1 ± 2.0 kcal. mole^{-1}. When Mn(s) is heated with $MnF_2(s)$, the lower fluoride, MnF, is produced. From equilibrium measurements, it has been possible to establish the dissociation energy of MnF(g) as $D°_{298} = 4.39 \pm 0.15$ e.v. (101.2 ± 3.5 kcal. mole^{-1}).

I. Introduction

In general, reliable Knudsen or Langmuir vaporization and sublimation rates for the transition metal halides have not been available. Brewer, Somayajulu, and Brackett[1] have reviewed the thermodynamic properties of the gaseous metal dihalides and presented measured or estimated heats of sublimation. More recently, Bautista and Margrave[2] have investigated the sublimation of a single crystal of MnF_2 in the temperature range 887 to 983°K. by the Langmuir technique using a vacuum microbalance.

The dissociation energies of the transition metal monofluorides are poorly known. The recent spectroscopic work on BeF[3] and BeCl[4] and thermochemical work on the alkaline earth fluorides[5,6] suggest that the stability of these molecules may be much greater than previously suspected. Herzberg[7] has tabulated recommended values for the dissociation energies of a large number of diatomic molecules and suggests a value of 3.9 e.v. for the MnF molecule.

In this work, the temperature range of observations has been extended, the vapor species identified, and the sublimation rate measured for MnF_2 by the Knudsen technique employing a mass spectrometer. In addition, the dissociation energy of the MnF molecule has been evaluated by utilizing the mass spectrometer to study the equilibrium $2MnF(g) = Mn(g) + MnF_2(g)$ in a Knudsen cell.

II. Experimental

The mass spectrometer employed in this work has been described previously.[5] The MnF_2 powder used in these experiments was obtained by crushing the single crystal material from the same sample as that used in the microbalance study of Bautista and Margrave.[2] The manganese metal powder was commercially available reagent grade. All samples were extensively outgassed in the instrument before temperature-dependence studies were begun.

III. Results and Discussion

The Sublimation and Evaporation of MnF_2.—Bautista and Margrave[2] investigated the sublimation of MnF_2 in the temperature range 887 to 983°K. by the Langmuir technique using a vacuum microbalance. From their data they calculated the heat of sublimation at 298°K. to be 76.4 ± 0.5 kcal. mole^{-1} by the third-law method and 76.0 ± 1.0 kcal. mole^{-1} by the second-law method. Free-energy functions for solid and gaseous MnF_2 were taken from Brewer, *et al.*,[1] who presented molecular parameters and thermodynamic data necessary for the calculations of the thermodynamic properties of gaseous metal dihalides. The MnF_2 molecule was assumed to be linear with a Mn–F bond distance of 1.72 Å. and the frequencies were given as $\omega_1 = 535$, $\omega_2(2) = 70$, and $\omega_3 = 696$ cm.$^{-1}$. The results of the microbalance study are shown in Fig. 1, together with the additional data obtained with the mass spectrometer.

The rates of sublimation and vaporization were measured and the vapor species identified between 1054 and 1193°K. by means of the mass spectrometric technique. The ionic species which were formed on electron bombardment of molecules effusing from the tantalum Knudsen cell were Mn^+, MnF^+, MnF_2^+, and lesser amounts of TaF_4^+. No dimers or higher polymeric species of MnF_2 were observed although the spectrum was scanned to mass 400.

Ionization efficiency curves for the ions Mn^+, MnF^+, and MnF_2^+ are presented in Fig. 2. In each case the measured ion intensity was corrected for background and photoionization effects.[8] Using as a standard the known value[9] of 10.4 e.v. for the ionization potential of mercury, one obtains appearance potentials for Mn^+, MnF^+, and MnF_2^+ equal to 7.7, 8.7, and 11.5 e.v., respectively, with an estimated uncertainty of ±0.3 e.v. The appearance potential of the Mn^+ ion when compared to the known[9] ionization potential of manganese, 7.4 e.v., indicates that this ion is probably due to simple ionization of Mn(g) which probably was formed by reaction of the sample with the tantalum crucible. The slight hump at about 12.0 e.v. was found to be reproducible and may be due to an excited state of the Mn^+ ion. The shape of the curve would seem to preclude the formation of Mn(g) by the dissociative ionization of $MnF_2(g)$. The low-energy tail of the MnF^+ ionization efficiency curve probably is due to simple ionization of the MnF(g) molecule while the break in the curve at *ca.* 14.5 e.v. is attributed to the onset of the process forming MnF^+ ions from $MnF_2(g)$ by dissociative ionization. The MnF_2^+ ion is attributed to simple ionization of $MnF_2(g)$.

The heat of sublimation of MnF_2 was determined from the experimentally observed ion currents of MnF_2^+ in the following manner. The intensity of the MnF_2^+ peak, using 75-v. electrons, was followed as a function of temperature between 1054 and 1128°K.

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[1] L. Brewer, G. R. Somayajulu, and E. Brackett, Lawrence Radiation Laboratory Report UCRL-9840, Sept., 1961; *Chem. Rev.*, **63**, 111 (1963).

[2] R. G. Bautista and J. L. Margrave, *J. Phys. Chem.*, **67**, 1564 (1963).

[3] V. M. Tatevskii, L. N. Tunitskii, and M. M. Novikov, *Opt. Spectry.* (USSR), **5**, 521 (1958).

[4] M. M. Novikov and L. N. Tunitskii, *ibid.*, **8**, 396 (1960).

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

[6] G. D. Blue, J. W. Green, T. C. Ehlert, and J. L. Margrave, *Nature*, **199**, 804 (1963).

[7] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

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

[9] C. E. Moore, National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1949.

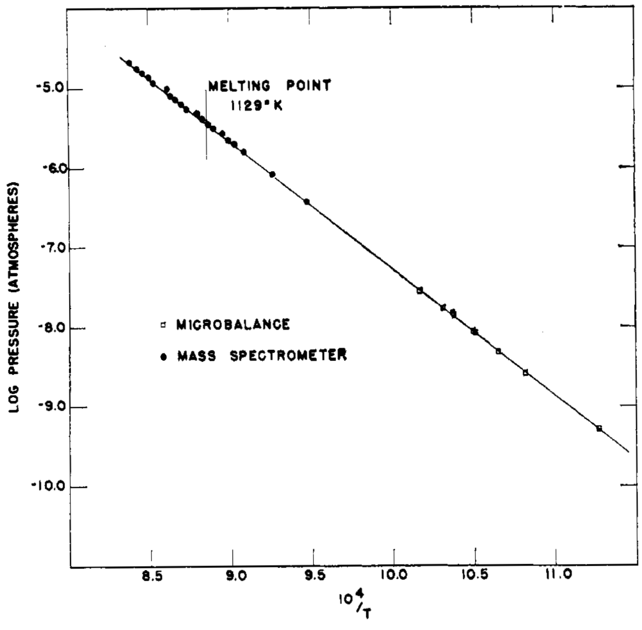

Fig. 1.—Vapor pressure data for MnF_2.

By making use of the ion current–pressure relationship $P = kI^+T$[10] and the integrated form of the Clausius–Clapeyron equation, a value of ΔH_T, which is independent of the proportionality constant k, may be found from the slope of the curve obtained by plotting log (I^+T) *vs.* $1/T$. The slope of this curve yielded a heat of sublimation of $\Delta H°_{1103} = 73.0 \pm 1.5$ kcal. mole^{-1}, where the uncertainty given is the standard deviation of the least-squares treatment. The true uncertainty may be two or three times this figure owing to such factors as temperature gradients in the crucible. When corrected to 298°K. using the heat-content values compiled by Mah[11] and the molecular constants listed by Brewer, *et al.*,[1] the second-law approach gives $\Delta H°_{298} = 76.5 \pm 1.5$ kcal. mole^{-1}. This value is in good agreement with the value 75 kcal. mole^{-1} estimated by Brewer.[1] The slope resulting from a plot of log (I^+T) *vs.* $1/T$ for the MnF^+ ion in the same temperature range, again using 75-v. electrons, yielded a heat of $\Delta H°_{1103} = 72.3 \pm 1.6$ kcal. mole^{-1} which agrees with the value obtained for MnF_2^+ within the limits of the standard deviations and further indicates that above 14.5 e.v. the major portion of the MnF^+ ions came from the dissociative ionization of $MnF_2(g)$.

A plot of log (I^+T) *vs.* $1/T$ for the ion MnF_2^+ in the temperature range 1132 to 1193°K. yielded a value for the heat of vaporization of $MnF_2(1)$ of $\Delta H°_{1159} = 71.9 \pm 2.4$ kcal. mole^{-1}. This data would indicate that the heat of fusion of MnF_2 is in the range 1–5 kcal. mole^{-1}, while Brewer[1] estimated 5.5 kcal. mole^{-1}. Unfortunately, the conditions[12] required for molecular flow limit the maximum temperature to about 1190°K., and the uncertainty resulting from measurements over the necessarily short temperature range is rather large as indicated by the standard deviation.

An alternative approach is to calculate $\Delta H°_{298}$ at each temperature from the absolute pressure and the free-energy function change for the reaction. The value of ΔH_T obtained in this study is the same as that obtained in the microbalance study, within the limits of experimental error, and hence the least-squares equations for log (I^+T) and log P as functions of temperature were combined to yield a value for the instrument constant k which was then combined with the experimental values of (I^+T) to calculate a value of P at each temperature. These pressures were then used for a third-law calculation of the heat of sublimation and yielded an average value of 76.1 ± 0.1 kcal. mole^{-1}.

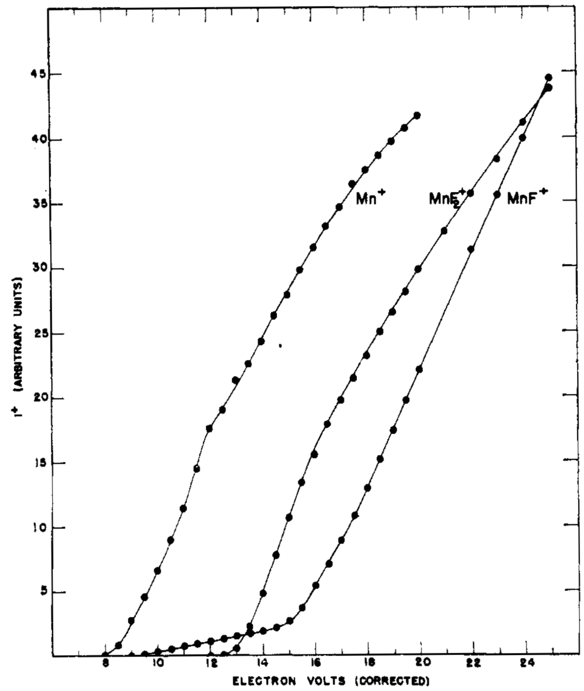

Fig. 2.—Ionization efficiency curves for species observed over MnF_2.

While the small standard deviation of ±0.1 kcal. mole^{-1} for the third-law heat reflects the high reproducibility of the measurements, the true uncertainty must reflect possible errors in entropy estimates, primarily for $MnF_2(g)$, as well as any errors introduced by the use of the microbalance data to compute the instrument constant k in order to determine the absolute pressures from the mass spectrometric data. The third-law heat of sublimation was therefore taken to be 76.1 ± 2.0 kcal. mole^{-1}. In using the second-law method to obtain the enthalpy of reaction, the major inherent errors are those in temperature measurement. The enthalpy correction for the gas is rather insensitive to the choice of molecular parameters. In practice, uncertainties of the order of ±3 kcal. mole^{-1} are obtained in the temperature range covered by this investigation. The second-law heat of sublimation may then be taken as 76.5 ± 3.0 kcal. mole^{-1}.

For calculating the pressure of $MnF_2(g)$ over solid MnF_2, the following equation has been derived.

$$\log P_{\text{atm}} = \frac{-(1.596 \pm 0.034) \times 10^4}{T} + 8.70 \pm 0.02$$

The Stability of the MnF Gaseous Molecule.—In order to achieve reducing conditions and enhance the amount of MnF(g) present, about 200 mg. of manganese powder was added to the MnF_2 sample in the Knudsen cell. The ionic species found to be due to

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

[11] A. D. Mah, U. S. Department of Interior, Bureau of Mines, Report of Investigation 5600, Director, Mines Bureau, Pittsburgh, Pa., 1960.

[12] K. D. Carlson, Argonne National Laboratory Report ANL 6156 (1960).

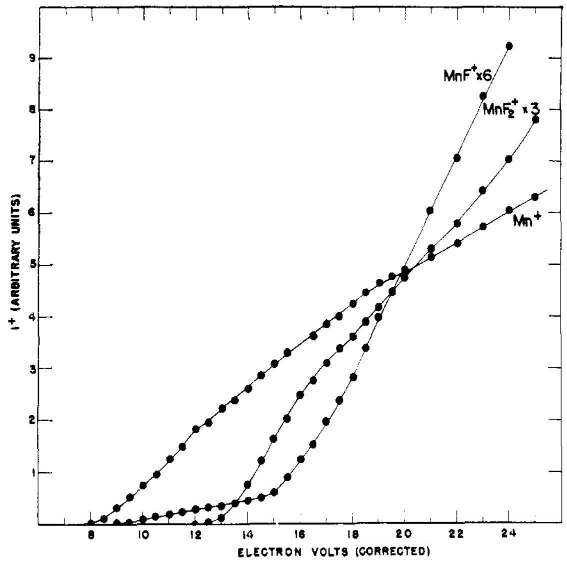

Fig. 3.—Ionization efficiency curves for species observed over MnF_2–Mn.

molecules effusing from the cell in the range 1089 to 1126°K. were Mn^+, MnF^+, and MnF_2^+. Ionization efficiency curves for these ions are shown in Fig. 3. Again, the measured ion intensities were corrected for background and photoionization effects.[8] Using the ionization potential of Hg equal to 10.4 e.v. as a standard,[9] one finds appearance potentials for Mn^+, MnF^+, MnF_2^+ equal to 7.5, 8.8, and 11.5 e.v., respectively, with an estimated uncertainty of ±0.3 e.v. The appearance potential of Mn^+ again indicates that this ion is due to the ionization of Mn(g), and the ionization efficiency curve again shows a "hump" at *ca.* 12 e.v. Temperature dependence studies of MnF^+ established that above the break at 14.5 e.v. the ion is produced by the dissociative ionization of MnF_2(g), whereas below 14.5 e.v. another process is involved which is assumed to be the simple ionization of MnF(g). In this system the activity of the MnF_2(s) was less than unity since the heat of formation from the condensed phase was greater than that found previously for the reaction $MnF_2(s) = MnF_2(g)$.

The equilibrium constant for the homogeneous reaction $2MnF(g) = Mn(g) + MnF_2(g)$ was determined at a series of temperatures using low-energy electrons. The use of electron voltages about 5 v. above the appearance potentials for the ions minimized the effects of fragmentation. The equilibrium constant, K_1, for this reaction is pressure independent so that instrument geometry and sensitivity factors cancel, and it was only necessary to correct the ion-current constant, $K_1' = I(MnF_2^+)I(Mn^+)/[I(MnF^+)]^2$, for relative cross sections, differences in energy above the threshold, and gains. The tabulated cross sections of Otvos and Stevenson[13] and experimental values of the gain ratios of the ions Mn^+, MnF^+, and MnF_2^+ were used to calculate $K_1 = 2.54K_1'$. The values of log K_1 then were used together with the free-energy functions for Mn(g) and MnF(g) from Kelley[14] and Kelley and King[15] and for MnF_2(g) from Brewer, *et al.*,[1] to calculate third-law heats of reaction at 298°K. The average value is $\Delta H°_{298} = -17.7 \pm 0.3$ kcal. mole^{-1}. The data and results are presented in Table I.

Table I

Equilibrium Constants and Heat for the Reaction

$2MnF(g) = Mn(g) + MnF_2(g)$

Temp., °K.	K_1'	log K_1	$\Delta(F°_T - H°_{298}/T)$, cal. deg.$^{-1}$ mole^{-1}	$\Delta H°_{298}$, kcal. mole^{-1}
1126	74.37	2.277	5.571	−18.0
1118	56.93	2.161	5.574	−17.3
1112	69.82	2.249	5.578	−17.6
1108	82.64	2.323	5.579	−18.0
1104	77.93	2.297	5.581	−17.8
1096	96.26	2.389	5.588	−18.1
1094	79.19	2.304	5.588	−17.6
1111	76.21	2.287	5.578	−17.8
1109	66.26	2.227	5.580	−17.5
1094	65.89	2.224	5.588	−17.2
1089	82.32	2.321	5.593	−17.7
			Average =	−17.7 ± 0.3

By combining the heat of sublimation, 76.1 kcal. mole^{-1}, with the known[11] heat of formation of MnF_2(s), together with the heat of sublimation of manganese[16] and the dissociation energy of fluorine,[17] one calculates the heat of atomization of MnF_2(g) to be 220.1 ± 5.5 kcal. mole^{-1} which is in good agreement with the value of 220 estimated by Brewer.[1] By combining the heat of dissociation for MnF_2(g) with the heat of reaction listed in Table I one obtains $D°_{298}$ (MnF) = 4.39 ± 0.15 e.v. From this value, the heat of formation of MnF(g) from the elements in their reference states at 298°K. was computed to be $\Delta H_f° = -13.4$ kcal. mole^{-1}. In comparison, the heat of formation of MnF_2(g) from the elements in their reference states at 298°K. was computed to be −113.4 kcal. mole^{-1}, in good agreement with the value of −115.0 kcal. mole^{-1} estimated by Brewer.[1]

It was not possible to determine the dissociation energy by measuring the heat of the heterogeneous reaction $2MnF(g) = Mn(g) + MnF_2(s)$ because, as pointed out previously, the activity of the MnF_2(s) in the Knudsen cell was less than unity.

One may independently determine an upper limit for the value of D(MnF) in the following manner. The intensities of the ions Mn^+ and MnF_2^+ are measured at some voltage much greater than the appearance potentials, in this experiment 75 v. The value of $I(MnF_2^+)$ must be corrected to account for that amount of MnF_2(g) undergoing dissociative ionization when exposed to 75-v. electrons. The intensity of the MnF^+ ion, measured at some value below the break at 14.5 e.v. is then extrapolated to 75 e.v. Calculating K_1' and K_1 for the reaction $2MnF(g) = Mn(g) + MnF_2(g)$ as before, one obtains $\Delta H°_{298} = -16.6 \pm 0.3$ kcal. mole^{-1} which leads to $D°_{298}(MnF) \leq 4.41 \pm 0.30$ e.v.

In a similar manner, one can set a lower limit on the value for D(MnF) by using the intensities of Mn^+ and MnF_2^+ at 75 e.v. as above and that of MnF^+ at 14.5 e.v., *i.e.*, assuming that the ionization efficiency curve levels off. Calculating K_1' and K_1 as before, one

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(13) J. W. Otvos and D. P. Stevenson, *J. Am. Chem. Soc.*, **78**, 546 (1956).

(14) K. K. Kelley, U. S. Department of Interior, Bureau of Mines Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960.

(15) K. K. Kelley and E. C. King, U. S. Department of Interior, Bureau of Mines Bulletin 592, U. S. Government Printing Office, Washington, D. C., 1961.

(16) H. Wiedemeier, *Z. anorg. allgem. Chem.*, **326**, 225 (1964).

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

obtains $\Delta H°_{298} = -27.3 \pm 0.3$ kcal. mole^{-1} and $D°_{298}$(MnF) $\geq 4.18 \pm 0.30$ e.v.

It was pointed out in the Introduction that the values of D(MnF) for the alkaline earth monofluorides obtained by means of the mass spectrometric technique are, in general, higher than the spectroscopic values reported in the literature. Such is the case for MnF also, although the difference is less than in the alkaline earth monofluorides.

The system Al–Mn–F has also been investigated in this laboratory.[18] In one experiment in which AlF_3(s) was heated with manganese powder, the species Mn(g), MnF(g), and MnF_2(g), in addition to aluminum-containing species, were observed to effuse from the Knudsen cell. The constant K_1' for the reaction $2MnF(g) = Mn(g) + MnF_2(g)$ was calculated for one temperature, 1070°K., and log K_1 was calculated to be -2.405. From this value, the heat of the reaction was found to be $\Delta H°_{298} = -17.7$ kcal. mole^{-1} which is identical with the result listed in Table I and thus supports 4.39 e.v. as the correct value for D(MnF).

Acknowledgments.—This work was supported by the United States Atomic Energy Commission, by the National Science Foundation, and by the Advanced Research Projects Agency through a contract administered by the U. S. Army Research Office, Durham.

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[18] T. C. Ehlert, unpublished work.

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Mass Spectrometric Studies at High Temperatures. VI. The Sublimation Pressure of Nickel(II) Fluoride

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RECEIVED JUNE 19, 1964

A mass spectrometric study has established the vapor species over NiF_2(s) as NiF_2(g). From temperature dependence studies by the Knudsen technique over the range 1054–1106°K., one derives the vapor pressure equation: $\log P_{\text{atm}} = -(1.690 \pm 0.028) \times 10^4/T + 10.17 \pm 0.01$. The errors quoted are standard deviations of the least-squares fit. The heat of sublimation for NiF_2 at 298°K. is 79.4 ± 1.0 kcal. mole^{-1}.

I. Introduction

Although nickel and high-nickel alloys are used extensively in equipment containing fluorine and highly reactive fluorides, relatively little is known about the sublimation rate and heat of sublimation of NiF_2. Glassner[1] evaluated the available thermochemical data for NiF_2 in the literature and presented recommended values, in part estimates. Brewer, Somayajulu, and Brackett[2] presented vaporization data and free-energy functions based on the work of Farber, Meyer, and Margrave.[3]

Glassner[1] reported the heat of vaporization at 2150° K. to be 55 kcal. mole^{-1}, which when corrected to 298° K. yielded a heat of sublimation, $\Delta H°_{298} = 83.2$ kcal. mole^{-1}. The results reported by Farber, *et al.*,[3] are shown in Fig. 1, together with the additional data obtained with the mass spectrometer. The data obtained in the Knudsen study of Farber yielded a second-law heat of sublimation at 1064°K. of about 96.5 kcal. mole^{-1}, and a third-law value of $\Delta H°_{298} = 78.7$ kcal. mole^{-1}. The two points obtained in the transpiration study of Meyer yielded a third-law value of 81.0 kcal. mole^{-1}. The combination of the data of Farber and Meyer yields a second-law heat of sublimation of about 60 kcal. mole^{-1}, and a third-law value of $\Delta H°_{298} = 79.4 \pm 1.5$ kcal. mole^{-1}. Brewer, *et al.*,[2] assumed the NiF_2 gaseous molecule to be linear with a Ni–F bond distance of 1.72 Å. and estimated the vibrational frequencies to be $\omega_1 = 550$ cm.$^{-1}$, $\omega_2(2) = 71$ cm.$^{-1}$, $\omega_3 = 707$ cm.$^{-1}$, and the heat of sublimation at 298°K. to be 78.5 kcal. mole^{-1}.

In this work, the vapor species has been identified and the heat of sublimation determined more precisely by measurements of the sublimation rate of NiF_2 by the Knudsen technique employing a mass spectrometer.

II. Experimental

The mass spectrometer employed in this work has been described previously.[4] The NiF_2 was commercially available reagent grade powder which was first heated at 800° for 6 hr. in an atmosphere of fluorine gas. The samples were extensively outgassed in the instrument before temperature dependence studies were begun.

The rates of sublimation were measured and vapor species identified between 1054 and 1106°K. by the mass spectrometric technique. The spectrum was scanned to mass 400 and the only ionic species found to be due to molecules effusing from the tantalum Knudsen cell were NiF_2^+, NiF^+, and Ni^+. The relative abundances of ions at masses 58 and 60, 77 and 79, and 96 and 98 were checked and found to correlate with the isotopic abundances of ^{58}Ni and ^{60}Ni.

Ionization efficiency curves for the observed ions are shown in Fig. 2. In each case the measured ion intensity was corrected for background and "photo" effects.[5] Using the known value[6] of 12.06 e.v. for the ionization potential of O_2, which is always present in small amounts as an impurity in the atmosphere of the apparatus, one obtains appearance potentials for NiF_2^+, NiF^+, and Ni^+ equal to 11.5, 13.0, and 16.7 e.v., respectively, with estimated uncertainties of ± 0.3 e.v. The appearance potentials and the shapes of the ionization efficiency curves for NiF^+ and Ni^+ indicate that these ions result from the dissociative ionization of NiF_2(g) and not from simple ionization of the species NiF(g) and Ni(g).

III. Results

Two independent methods were employed to determine the heat of sublimation of NiF_2 from the experimentally observed ion currents of NiF_2^+. The intensity of the $^{58}NiF_2^+$ peak, using 75-v. electrons,

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[1] A. Glassner, Argonne National Laboratory Report ANL 5750, Jan., 1958.

[2] L. Brewer, G. R. Somayajulu, and E. Brackett, Lawrence Radiation Laboratory Report UCRL-9840, Sept., 1961; *Chem. Rev.*, **63**, 111 (1963).

[3] M. Farber, R. T. Meyer, and J. L. Margrave, *J. Phys. Chem.*, **62**, 883 (1958).

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

[5] W. A. Chupka and M. G. Inghram, *ibid.*, **59**, 100 (1955).

[6] A. J. C. Nicholson, *ibid.*, **67**, 954 (1963).