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 AlF₃(s) was heated with manganese powder, the species Mn(g), MnF(g), and MnF₂(g), in addition to

(18) T. C. Ehlert, unpublished work.

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).

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

BY T. C. EHLERT, R. A. KENT, AND J. L. MARGRAVE

A mass spectrometric study has established the vapor species over NiF₂(s) as NiF₂(g). From temperature dependence studies by the Knudsen technique over the range 1054–1106°K., one derives the vapor pressure equation: $\log P_{atm} = -(1.690 \pm 0.028) \times 10^4/T + 10.17 \pm 0.01$. The errors quoted are standard deviations of the least-squares fit. The heat of sublimation for NiF₂ 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 NiF₂. Glassner[1] evaluated the available thermochemical data for NiF₂ 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 NiF₂ 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 NiF₂ by the Knudsen technique employing a mass spectrometer.

II. Experimental

The mass spectrometer employed in this work has been described previously.[4] The NiF₂ 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 NiF₂⁺, 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 ⁵⁸Ni and ⁶⁰Ni.

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 O₂, which is always present in small amounts as an impurity in the atmosphere of the apparatus, one obtains appearance potentials for NiF₂⁺, 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 NiF₂(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 NiF₂ from the experimentally observed ion currents of NiF₂⁺. The intensity of the ⁵⁸NiF₂⁺ peak, using 75-v. electrons,

(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).

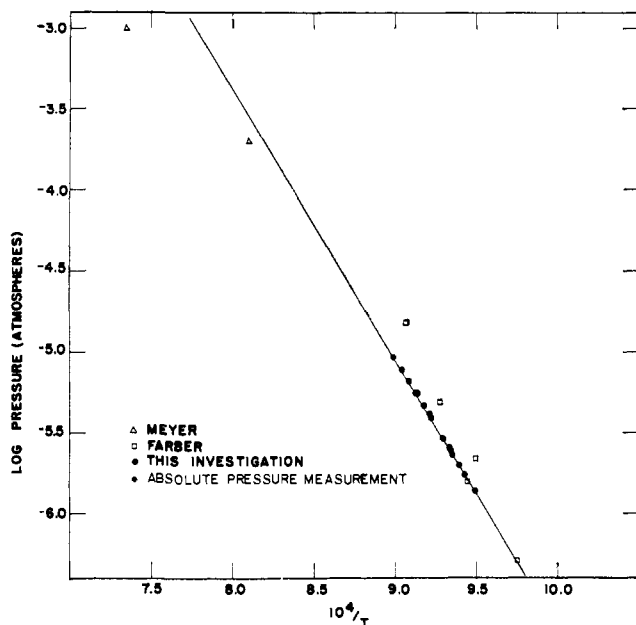(6) A. J. C. Nicholson, *ibid.*, **67**, 954 (1963).

Fig. 1.—Vapor pressure data for NiF_2 by various investigators.

was followed as a function of temperature. By making use of the ion current–pressure relationship[7] $P = kI^+T$ 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 plot yielded a heat of sublimation of $\Delta H°_{1080} = 77.3 \pm 1.3$ kcal. mole^{-1}, where the uncertainty given is the standard deviation of the least-squares treatment. When corrected to 298°K. using the heat content equations estimated by Glassner,[1] the second-law approach gives $\Delta H°_{298} = 79.5 \pm 1.3$ kcal. mole^{-1}. Similar plots of log (I^+T) vs. $1/T$ for the ions $^{58}NiF^+$ and $^{58}Ni^+$ yielded the values $\Delta H°_{1092} = 77.7$ and $\Delta H°_{1081} = 81.0$ kcal. mole^{-1}, respectively. These values agree with the value found for $^{58}NiF_2^+$ within the range of experimental precision and give further indication that the NiF^+ and Ni^+ are formed by the dissociative ionization of $NiF_2(g)$.

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. In order to determine the instrument constant, k, a weighed sample of previously degassed NiF_2 was vaporized from the crucible at a constant temperature, and the intensity of the $^{58}NiF_2^+$ peak was followed as a function of time. At 1112°K., 8.4×10^{-3} g. effused in 333 min. By use of the Knudsen equation, the pressure was calculated to be 9.4×10^{-6} atm. The value of k thus determined was combined with the least-squares equation for log (I^+T) as a function of reciprocal temperature to yield the following vapor pressure equation.

$$\log P_{atm} = -(1.690 \pm 0.028) \times 10^4/T + 10.17 \pm 0.01$$

The k value 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 $NiF_2(s)$ and $NiF_2(g)$ taken from Brewer, et al.,[2] to obtain a third-law heat of sublimation. The results of the

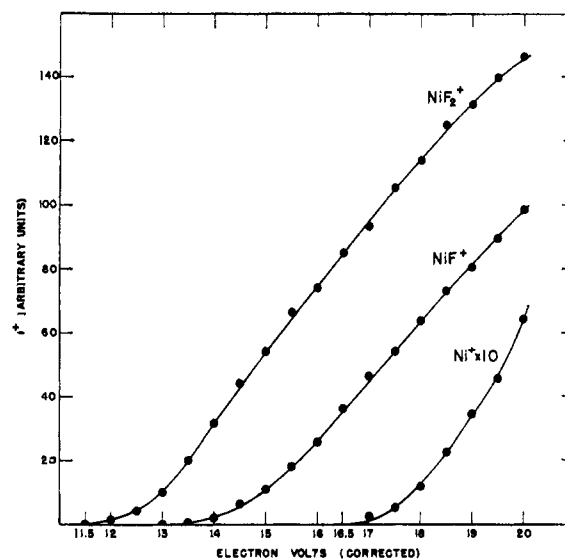(7) W. A. Chupka and M. G. Inghram, *J. Chem. Phys.*, **21**, 371 (1953).

mass spectrometric runs are presented in Table I and plotted in Fig. 1.

While the small standard deviation of ± 0.05 kcal. mole^{-1} for the third-law heat reflects the high reproducibility of the measurements, the true uncertainty must reflect errors in the estimated thermodynamic functions, particularly for $NiF_2(g)$. The slight tem-

Fig. 2.—Ionization efficiency curves for species observed over NiF_2.

TABLE I

Temp., °K.	$I(NiF_2^+)$,[a] arbitrary units	$-\text{Log } P_{atm}$	$-\Delta(FT° - H°_{298}/T)$, cal. deg.$^{-1}$ mole^{-1}	$\Delta H°_{298}$, kcal. mole^{-1}
1101	23.4	5.180	48.31	79.28
1095	18.0	5.263	48.34	79.30
1090	14.0	5.334	48.36	79.31
1085	12.6	5.406	48.38	79.34
1071	8.82	5.609	48.45	79.43
1065	6.75	5.698	48.48	79.40
1061	6.24	5.758	48.50	79.41
1095	26.7	5.263	48.34	79.30
1072	13.7	5.594	48.45	79.37
1054	8.70	5.864	48.53	79.43
1106	44.6	5.111	48.28	79.26
1086	27.9	5.391	48.38	79.33
1076	18.0	5.536	48.43	79.37
1069	9.80	5.638	48.46	79.38

Average $= 79.35 \pm 0.05$

[a] Second set of measurements (last seven points) corrected for change in multiplier gain.

perature dependence of the third-law values of the heat of sublimation probably indicates a small error in the estimated free-energy functions and, hence, the third-law heat is 79.4 ± 1.0 kcal. mole^{-1}. The major inherent errors in the second-law results are those in temperature measurement. In practice, uncertainties of the order of ± 3 kcal. mole^{-1} are usual in the temperature range covered by this investigation, and the second-law heat of sublimation at 298°K. is 79.5 ± 3.0 kcal. mole^{-1}. The third-law results obtained in this investigation agree with those obtained in the previous studies,[3] while the second-law values do not. The transpiration data of Meyer consists of only two points, and the low values for the pressure of $NiF_2(g)$ are most likely due to incomplete saturation of the carrier gas. The most likely causes of the increased

second-law value in the Knudsen study of Farber are errors in temperature measurement.

With the heat of formation of NiF_2[8] equal to -156 ± 2 kcal. mole^{-1}, the heat of sublimation of Ni[9] equal to 102.67 ± 1.40 kcal. mole^{-1}, and the atomization energy of fluorine[10] equal to 37.7 ± 0.1 kcal. mole^{-1}, one derives a dissociation energy of NiF_2 into atoms of

(8) K. S. Pitzer and L. Brewer, revision of G. N. Lewis and M. Randall, "Thermodynamics," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(9) R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley and Sons, Inc., New York, N. Y., 1963.

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

217.0 kcal. mole^{-1} and an average Ni–F bond energy of 108.5 kcal. mole^{-1} (4.71 e.v.). The alternate heat of sublimation for Ni listed by Nesmeyanov,[11] which would seem to be incorrect in view of other values[9] listed in the literature, leads to an average Ni–F bond energy of 4.22 e.v. There are no optical spectroscopic data on $NiF(g)$ or $NiF_2(g)$ for comparison.

(11) A. N. Nesmeyanov, "Vapor Pressure of the Chemical Elements," Elsevier Publishing Co., New York, N. Y., 1963.

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The Photochemistry of Uranyl Oxalate[1]

BY D. H VOLMAN AND J. R. SEED

The photolysis of aqueous solutions of uranyl oxalate–oxalic acid was studied at various intensities, wave lengths, temperatures, concentrations, and acidities. The results are interpreted by the stoichiometrical relations: (1) $H_2C_2O_4 \rightarrow CO + CO_2 + H_2O$; (2) $H_2C_2O_4 \rightarrow CO_2 + HCOOH$; and (3) $U^6 + H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + U^4$. The fraction of decomposition attributable to each pathway was found to be independent of intensity, wave length, and temperature and to depend on concentration and acidity. Quantum yields of gaseous product formation were evaluated for various experimental conditions. Mechanisms for (1) and (2) are given using the simplest uranyl complexes, $UO_2(HC_2O_4)^+$ and $UO_2(C_2O_4)$. For (3) a mechanism is given which accounts for the products by single electron-transfer steps and disproportionation of U^V to U^{IV} and U^{VI}.

Introduction

For studies of photochemical reactions in aqueous solutions using volumes in the range of 1 to 10 μl., it was necessary to have a suitable actinometric system. Consequently, we developed a simplified method of uranyl oxalate actinometry.[2] The actinometry is based on the determination of CO by flame-ionization gas chromatography after catalytic hydrogenation to methane.[3] The method was more sensitive than reported for any other chemical actinometer known to us.

The reaction usually given[4] for the photodecomposition of oxalic acid in uranyl oxalate actinometry is

$$H_2C_2O_4 \longrightarrow H_2O + CO_2 + CO \qquad (1)$$
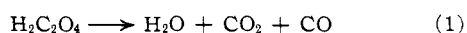
From this equation, it appears that it should be possible to relate the CO yield to the oxalate decomposition and, hence, to the light absorbed. This reaction, however, does not represent the experimentally determined stoichiometry. Carter and Weiss[5] considered also the reactions

$$H_2C_2O_4 \longrightarrow HCOOH + CO_2 \qquad (2)$$

$$H_2C_2O_4 + U^6 \longrightarrow H_2O + 2CO_2 + U^4 \qquad (3)$$
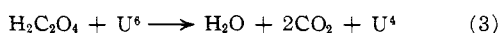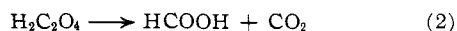
They observed that the relative proportions of reactions 1, 2, and 3 depend upon the acidity of the solution and the concentration of quenching ion present. Nevertheless, it seemed feasible to establish a relationship between the quantum yield of CO formation and that

(1) Supported by the U. S. Army Research Office, Durham.

(2) K. Porter and D. H. Volman, J. Am. Chem. Soc., 84, 2011 (1962).

(3) K. Porter and D. H. Volman, Anal. Chem., 34, 748 (1962).

(4) C. M. Masson, V. Boekelheide, and W. A. Noyes, Jr., in "Catalytic Photochemical, Electrolytic Reactions" ("Technique of Organic Chemistry," Vol. 2), 2nd Ed., A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, pp. 294, 295.

(5) A. H. Carter and J. Weiss, Proc. Roy. Soc. (London), A174, 351 (1940).

of oxalate decomposition. In our earlier work, we established the relationship for a limited range of conditions.

The present work was initiated because of our interest in further development of the actinometric method. It soon became apparent, however, that the problem had inherent photochemical interest aside from actinometry. A major emphasis of this work, therefore, has been on the photochemistry of uranyl oxalate systems.

Experimental

Apparatus.—Experiments using 2537-Å. radiation were carried out in the manner we have previously described,[6] using a helical mercury resonance arc. The reaction cell was a cylindrical quartz tube, 20-mm. diameter, in which stirring was accomplished by an induction method. For other wave lengths, a Pyrex cell, 42-mm. diameter and 35 mm. deep, with plane parallel windows was used. The light source for these experiments was a medium-pressure mercury arc, UA-3 GE 360-w. lamp. For 3660-Å. radiation, Corning filter No. 7-39 was used. For 4350-Å. radiation, an Optics Technology Monopass interference filter was used.

Materials.—Triply distilled water was used in all experiments. Oxalic acid, Mallinckrodt reagent, was recrystallized three times from water, centrifuged, and dried over calcium chloride. Uranyl oxalate was prepared by treating a hot solution of uranyl nitrate with excess oxalic acid. The solution was cooled, the resulting precipitate was centrifuged, washed, and dried, and the optical density at 2537 Å. was measured. The uranyl oxalate was recrystallized from water and the optical density remeasured. After a third recrystallization, no change in optical density was observed. Some uranyl oxalate was also prepared from commercial uranous oxalate. The uranous salt was oxidized by hot concentrated nitric acid to uranyl and then treated in the manner described above. Uranyl formate was prepared by reacting formic acid with uranyl oxide.

Analysis.—Oxalate was determined by titration with potassium permanganate. Gaseous products, carbon monoxide and carbon

(6) D. H. Volman and L. W. Swanson, J. Am. Chem. Soc., 82, 4141 (1960).