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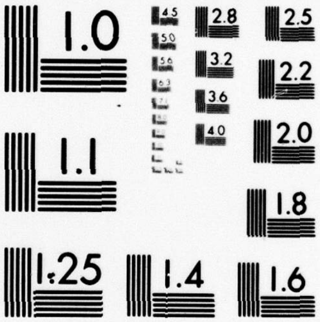
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DISSOCIATION ENERGIES AND HEATS OF FORMATION OF GASEOUS METALLIC HALIDES

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for the period
1 May 1974 through 30 April 1979

Contract F44620-74-C-0075

Prepared for
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Bolling Air Force Base, D. C. 20332

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Prepared by:

Milton Farber
Principal Investigator

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HEATS OF FORMATION	SILICON BROMIDES
SILANE FLUORIDES	SILICON CHLORIDES
SILANE BROMIDES	ALKALINE EARTH OXIDES
SILANE CHLORIDES	MAGNESIUM CHLORIDE

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This report summarizes the experimental thermodynamic data obtained, including dissociation energies and heats of formation, for the species BaO, MgO, CaO, SrO, NiO, MgCl, SiCl, $SiCl_2$, $SiCl_3$, SiF_2, SiF_3, SiBr, $SiBr_2$ $SiBr_3$, SiH_2F_2, SiF, SiH_3F, $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, $SiHBr_3$, SiH_2Br_2, SiH_3Br and $SiHF_3$.

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1. INTRODUCTION

This report presents a summary of experimental thermodynamic data obtained under Contract F44620-74-C-0075 during the period 1 May 1974 through 30 April 1979 in support of Air Force propulsion and materials programs, as well as laser weapons technology requirements. The results have been published or are in the process of publication in international scientific journals. In addition, the data have been incorporated in numerous up-dated or new JANAF Thermochemical Tables.

Reliable data for the gas phase reactions of the diatomic metal compounds are required to assess accurately the candidate species which are potentially significant to chemical laser technology for use by the Air Force involving weaponry and defense systems, as stated previously. Prior to these studies the dissociation energies for a number of diatomic oxides and halides were undetermined or uncertain. Thus experiments were conducted to obtain data with a high degree of accuracy for certain alkaline earth species considered important to the required technology. Energies of dissociation were determined for several diatomic alkaline earth oxides and nickel oxide. Thermodynamic data were also obtained for the silicon and magnesium halides. The silane halides, fluorides, chlorides and bromides were also investigated. For many of the compounds the data obtained in these studies were the first reported experimental results. In addition to the experimental investigations for the species mentioned, review articles were published involving the Group 2 and Group 3 oxides and the controversial AlO_2 species.[1,2,3]

The following sections include a brief summary of the work accomplished and lists of literature publications and presentations at international scientific meetings.

2. WORK ACCOMPLISHED

During the contract period experimental thermodynamic data were obtained for the following compounds and species: BaO, MgO, CaO, SrO, NiO, MgCl, SiCl, $SiCl_2$, $SiCl_3$, SiF, SiF_2, SiF_3, SiBr, $SiBr_2$, $SiBr_3$, $SiHF_3$, SiH_2F_2, SiH_3F, $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, $SiHBr_3$, SiH_2Br_2 and SiH_3Br.

These data, with the exception of those for the silane chlorides and silicon bromides, have been published in the open literature. Heats of formation and dissociation energy values for these species, as well as the appropriate publication number as cited in Section 3, are presented in Table 1. Papers involving the silane chlorides and silicon bromides are in the process of publication. A summary of the results obtained for these latter species is presented in the following sections.

A. Heats of Formation of the Silane Chlorides, $SiHCl_3(g)$, $SiH_2Cl_2(g)$, and $SiH_3Cl(g)$

Effusion-mass spectrometric second and third law reaction enthalpies were obtained for $SiCl_4(g) + H_2(g) = SiHCl_3(g) + HCl(g)$ in the temperature range 1155 to 1500 K. The reactions $SiHCl_3(g) + H_2(g) = SiH_2Cl_2(g) + HCl(g)$ and $SiH_2Cl_2(g) + H_2(g) = SiH_3Cl(g) + HCl(g)$ in the temperature range 900 to 1200 K were also studied. From the heats of reaction third law ΔH_{f298} values of -119.3 ± 0.5, -75.3 ± 1.0 and -32.4 ± 1.5 kcal/mole were obtained for $SiHCl_3(g)$, $SiH_2Cl_2(g)$ and $SiH_3Cl(g)$, respectively.

This appears to be the first effusion-mass spectrometric study, although several calorimetric and vapor investigations have been reported. The vapor pressure of $SiHCl_3(l)$ was determined by Jenkins and Chambers,[4] by Booth and Stillwell,[5] and by Stock and Zeidler.[6] From electron impact studies Steele, et al,[7] reported -110 ± 5 kcal/mole for the ΔH_{f298} of $SiHCl_3(g)$. Wolf[8] reported -117.4 ± 1.7 kcal/mole from solution calorimetry experiments. Reuther[9] obtained -112 kcal/mole from oxygen bomb calorimetry studies. The JANAF Tables dated December 31, 1976,[10] employing their own revised auxiliary data and those of Wagman, et al,[11] revised the values of Reuther and Wolf to -115 and -124 kcal/mole, respectively.

Sirtl, et al,[12] made computer calculations from equilibria reaction data involved in the production of silicon crystals for the semiconductor field. From these data they obtained -116.9 ± 1 kcal/mole for the ΔH_{f298}. The JANAF Tables,[10] employing a value for the ΔH_{f298} of $SiCl_4(g)$ 1.8 kcal/mole more negative than that used by Sirtl, et al,[12] revised their value to -118.8 ± 1 kcal/mole for the ΔH_{f298} of $SiHCl_3(g)$ in the table dated December 31, 1976. This is essentially identical to the third law value of -119.3 ± 0.5 kcal/mole obtained at this laboratory.

Although experimental conditions were not identical, Sirtl, et al,[12] reported an $SiHCl_3(g)/SiH_2Cl_2(g)$ ratio of ~ 20 from computer calculations at 1000 K involving a Cl/H ratio of 0.1 and a system pressure of 0.1 atm. This is fairly close to the ratio of ion intensities observed in these experiments at 993 K. Seiter and Sirtl,[13] using linear interpolations between $SiCl_4(g)$ and $SiH_4(g)$, reported a value of -75 kcal/mole for the ΔH_{f298} of $SiH_2Cl_2(g)$. It is suggested in the JANAF Tables[10] that ΔH_f values show minor deviations from linearity for the chlorosilanes and that the ΔH_f has a cubic variation with a constant third difference of -1.5 kcal/mole; thus a value of -76.6 ± 3 kcal/mole for the ΔH_{f298} of $SiH_2Cl_2(g)$ is recommended.[10]

An estimate of -34 kcal/mole for the ΔH_{f298} of $SiH_3Cl(g)$ was calculated from a linear interpolation of bond strengths of $SiCl_4(g)$ and $SiH_4(g)$.[13] The JANAF Tables,[10] using the non-linearity correction of -2.5 kcal/mole estimate -33.9 ± 2 kcal/mole for the ΔH_{f298} of $SiH_3Cl(g)$.

B. Heats of Formation of the Silicon Bromides $SiBr(g)$, $SiBr_2(g)$, and $SiBr_3(g)$

An effusion-mass spectrometric study of the reaction of $SiBr_4(g)$ with Si(c) in the temperature range 1054 to 1603 K has been completed. Second and third law reaction enthalpies were obtained for $SiBr_4(g) + Si(c) = 2SiBr_2(g)$, $SiBr_4(g) + SiBr_2(g) = 2SiBr_3(g)$, and $SiBr_2(g) + Si(c) = 2SiBr(g)$. From the heats of reaction third law ΔH_{f298} values of 103.5 ± 2.5, -10.5 ± 1 and -48.0 ± 0.5 kcal/mole were obtained for SiBr(g), $SiBr_2(g)$ and $SiBr_3(g)$, respectively. For the dissociation of SiBr(g) $\longrightarrow$ $(^3P_0)Si(g) + (^3P_{3/2})Br(g)$ a third law dissociation energy value of 87.0 ± 2.5 kcal/mole was calculated.

Two previous transpiration, or flow, experiments involving $SiBr_2(g)$ have been reported. Schafer, et al[14] obtained 71.5 ± 1 kcal/mole for the reaction, $SiBr_4(g) + Si(c) = 2SiBr_2(g)$, whereas Wolf[15] reported 79.9 ± 2 kcal/mole. He reduced his data and obtained a ΔH_{f298} value of -10.0 ± 2 kcal/mole for $SiBr_2(g)$. The JANAF Tables[10] recommend an average of -12.5 ± 4 kcal/mole from the data of the two flow studies. It was assumed in these flow experiments that $SiBr_2(g)$ was the only product from the reaction. In the temperature range of the two experiments, 1200 to 1500 K, the mass spectrometer intensities indicate that the $SiBr_3(c)$ concentration may be as much as 10% that of the $SiBr_2(g)$ at 1200 K and 2% at 1500 K, although the flow experiments assumed the product of the reaction to be entirely $SiBr_2(g)$. This may partially account for the apparent greater stability (approximately 2 kcal/mole) in the value for the heat of formation of $SiBr_2(g)$ obtained in the flow studies over that of the current mass spectrometer experiments.

Several values for the dissociation energy for SiBr have been reported, although this appears to be the first thermochemical value. Gaydon and Krasnov reported 81 ± 12 and 85 ± 17 kcal/mole, respectively.[16,17] Kuznetsova and Kuzyakov,[18] from a linear Birge Sponer extrapolation, obtained 85.8 ± 11.4 kcal/mole, which is in close agreement with the theoretical treatment by Tandon and Tandon,[19] who reported 85.3 kcal/mole. The JANAF Tables[10] corrected the value for the ionic bond characteristics and adopted 77.3 ± 10.3 kcal/mole. Our mass spectrometric result of 87.0 kcal/mole for the D_0 of SiBr, which is in agreement with the linear Birge Sponer extrapolations, indicates that very little ionic bonding exists in this molecule.

3. LIST OF PUBLICATIONS

1. "The Dissociation Energies of Calcium Oxide and Strontium Oxide," High Temp. Sci. 8, 73 (1976).

2. "The Dissociation Energy of Magnesium Oxide," High Temp. Sci. 8, 195 (1976).

3. "The Dissociation Energy of Barium Oxide," High Temp. Sci. 7, 74 (1975).

4. "The Dissociation Energy of NiO and Vaporization and Sublimation Enthalpies of Ni," Analytical Calorimetry, Vol. 3, Plenum Press, 1974, p. 731.

5. "The Dissociation Energy of Magnesium Chloride," Chem. Phys. Letts., 42, 567 (1976).

6. "Mass Spectrometric Determination of the Heats of Formation of the Silicon Subchlorides SiCl(g), $SiCl_2$(g) and $SiCl_3$(g)," J. Chem. Soc., Faraday Trans. I, 73, 1672 (1977).

7. "Mass Spectrometric Determination of the Heats of Formation of the Silicon Fluorides SiF(g), SiF_2(g) and SiF_3(g)," J. Chem. Soc., Faraday Trans. I, 74, 1089 (1978).

8. "Mass Spectrometric Determination of the Heats of Formation of the Silicon Bromides SiBr(g), $SiBr_2$(g) and $SiBr_3$(g)," submitted for publication, High Temperature Science.

9. "Mass Spectrometric Determination of the Heats of Formation of the Silane Fluorides," Chem. Phys. Letts. 51, 307 (1977).

10. "Heats of Formation of the Silane Chlorides," in press, Journal of Chemical Thermodynamics.

11. "Mass Spectrometric Determination of the Heats of Formation of the Silane Bromides," Chem. Phys. Letts. 60, 216 (1979).

4. PRESENTATIONS AT SCIENTIFIC MEETINGS

1. "Thermochemical Reactions of Aluminum and Fluorine in Hydrogen-Oxygen Flames," Fourth International Conference on Chemical Thermodynamics, Montpellier, France, August 1975. (Proceedings, Vol. III, p. 34).

2. "Thermochemical Reactions of Silicon with SiF_4 and $SiCl_4$," Fifth International Conference on Chemical Thermodynamics, Ronneby, Sweden, August 1977.

3. "Heats of Formation of Gaseous Metallic Halides and Oxides," 1978 Joint AFOSR/AFRPL Rocket Propulsion Research Meeting, Lancaster, California, April 1978.

Table 1

HEAT OF FORMATION AND DISSOCIATION ENERGY VALUES

Compound	ΔH_{f298} (kcal/mole)	D_o (kcal/mole)	Publication from Section 3
BaO	-28.3 ± 0.3	129.7 ± 0.3	3
MgO	8.1 ± 0.5	85.7 ± 0.5	2
CaO	10.1 ± 0.2	91.4 ± 0.2	1
SrO	-0.5 ± 0.2	98.3 ± 0.2	1
NiO	76.3 ± 1.5	83.5 ± 1.5	4
MgCl	-13.9 ± 0.5	77.4 ± 0.5	5
SiCl	47.1 ± 0.6	88.6 ± 0.6	6
$SiCl_2$	-40.6 ± 0.6		6
$SiCl_3$	-93.3 ± 0.5		6
SiF	-5.8 ± 0.5	131.2 ± 0.5	7
SiF_2	-140.6 ± 0.3		7
SiF_3	-259.3 ± 0.5		7
SiBr	103.5 ± 2.5	87.0 ± 2.5	8
$SiBr_2$	-10.5 ± 1.0		8
$SiBr_3$	-48.0 ± 0.5		8
$SiHF_3$	-293.0 ± 2.0		9
SiH_2F_2	-192.2 ± 2.0		9
SiH_3F	-99.4 ± 2.0		9
$SiHCl_3$	-119.3 ± 0.5		10
SiH_2Cl_2	-75.3 ± 1.0		10
SiH_3Cl	-32.4 ± 1.5		10

Table 1 - continued

$SiHBr_3$	-72.5 ± 1.0	11
SiH_2Br_2	-43.2 ± 1.5	11
SiH_3Br	-15.3 ± 0.5	11

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