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FIRST QUARTERLY LETTER REPORT

✓ THERMODYNAMIC PROPERTIES OF PROPELLANT
COMBUSTION PRODUCTS

ARPA Order No. 317, Task 13
ARPA Code 4910

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Contract . 49(638)-1397, Dated 1 April 1964

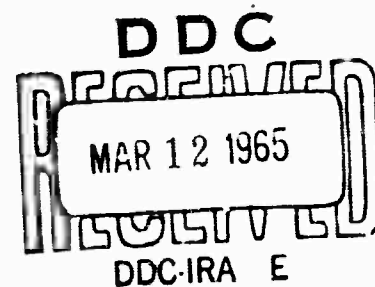
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Project Scientist: D. L. Hildenbrand, ORiole 5-1234, Ext. 1989

Report Period: 1 May - 15 July 1964

Approved by: S. W. Weller
S. W. Weller, Director
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INTRODUCTION

The objective of this program is to provide thermodynamic data for species which are potentially important combustion products of advanced chemical propulsion systems. Enthalpy and entropy data for species of interest are obtained from equilibrium studies carried out by effusion and free-evaporation techniques, and by high-temperature mass spectrometry. These experimental techniques and a number of results obtained to date have been described in detail in publications and technical progress reports generated under Contracts NOrd 17980, Task 3, and NOw 61-0905-c, Task C.

TECHNICAL PROGRESS

I. Heat of Sublimation of Boron

Torsion-Langmuir measurements of the vapor pressure of crystalline boron were completed. Some preliminary results on this system were reported earlier.¹ Vapor pressures were evaluated from measurement of the recoil force of free-surface vaporization from high-purity (99.999 percent) boron discs mounted on graphite, tantalum and tungsten sample holders, using the torsion techniques. From studies of the vaporization rate as a function of sample surface area, it was shown that corrections for reflection of vaporized atoms back to the surface were negligible. In addition, the vaporization rate was found to be essentially independent of surface roughness, indicating a near-unit vaporization coefficient. X-ray diffraction analyses of the sample surfaces after the measurements showed no contamination with boron carbide or metal borides.

A third-law analysis yielded the following boron heats of sublimation: graphite holder (1950 to 2140°K), $\Delta H_{298} = 136.4 \pm 0.2$ kcal/mole; tantalum holder (1950 to 2030°K), $\Delta H_{298} = 135.8 \pm 0.3$ kcal/mole; and tungsten holder (1960 to 2060°K), $\Delta H_{298} = 136.0 \pm 0.2$ kcal/mole. Uncertainties are average deviations. The second-law slope, considering all the data, gave $\Delta H_{2030} = 134.7 \pm 3$ and $\Delta H_{298} = 136.3 \pm 3$ kcal/mole with the uncertainties being estimated accuracies. These heats obtained from free-evaporation measurements are in good agreement with the corresponding value $\Delta H_{298} \text{ (sub)} = 135.7 \pm 1.3$ for boron derived from effusion measurements of the boron decomposition pressure over boron carbide.²

II. Gaseous Dihalides

To obtain more definitive information about the thermodynamic properties of metal dihalide vapor molecules as a class of compounds, the vapor pressures of strontium, barium and cadmium chlorides were measured by the torsion-effusion method. In addition, the mass spectrum of saturated cadmium chloride vapor was studied in detail.

Cadmium chloride showed a small effusion hole-size effect, indicating a condensation coefficient slightly less than unity. The vapor mass spectrum indicated less than a few tenths of a percent of dimer or higher polymers at molecular effusion pressures. Equilibrium vapor pressures deduced from the effusion data covering the range 670 to 760°K, when extrapolated to the melting point (842°K), were in close agreement with transpiration data in the literature. The effusion and transpiration data together yielded the second-law values $\Delta H = 39.9$ kcal/mole and $\Delta S = 35.8$ cal/mole deg for the sublimation of CdCl_2 at 750°K. These data provide an especially good opportunity to estimate the previously unobserved bending frequency of $\text{CdCl}_2(\text{g})$, since the entropy of $\text{CdCl}_2(\text{c})$ is known accurately from thermal measurements, the asymmetric stretching frequency has been observed, the Cd-Cl distance is known, and it is fairly certain that the molecule is linear. Taking the doubly degenerate bending frequency as an adjustable parameter, it is found that an ω_2 value of 95 cm^{-1} is required to give agreement between calculated and experimental entropies. A bending frequency of this magnitude is in agreement with conclusions drawn from data on other dihalides³ and indicates that a bending-to-stretching force constant ratio of about 0.01 to 0.03 is reasonable for the Group II dihalides.

Concordant vapor pressure data were obtained for SrCl_2 and BaCl_2 with graphite and platinum effusion cells. These two substances have nearly identical vapor pressures, both as regards magnitude and slope, with the SrCl_2 about 15 percent lower than the BaCl_2 pressures. Earlier BaCl_2 data⁴ appear to be in serious error. A preliminary analysis of the data gave values of $-\log P$ (atm) of 5.90, 4.95 and 4.13 for SrCl_2 at 1200, 1300 and 1400°K, respectively, and 5.35, 4.45 and 3.67 for BaCl_2 at 1250, 1350 and 1450°K, respectively. All data are on the liquid phases. These data, together with earlier effusion data on liquid CaCl_2 ,⁵ join smoothly with recent boiling point data⁶ in the millimeter range for

CaCl_2 , SrCl_2 and BaCl_2 , and show that the entropies of vaporization of SrCl_2 and BaCl_2 , while nearly equivalent, are about 4.2 cal/mole deg higher than that of CaCl_2 at the same temperature and pressure. This result is in agreement with electric deflection studies⁷ which showed SrCl_2 and BaCl_2 to be polar (bent) molecules and CaCl_2 to be a nonpolar (linear) molecule, since the entropy of a linear molecule is about 4.5 cal/mole deg lower than that of the corresponding bent molecule with a 100 to 150 degree bond angle. Because the entropies of $\text{SrCl}_2(\text{c})$ and $\text{BaCl}_2(\text{c})$ at 298°K are not available, it is not possible to derive experimental values for the absolute entropies of the gaseous molecules. However, complete entropy data are available for condensed CaCl_2 , and these data together with the vaporization data indicate a bending frequency of about 60 cm^{-1} for $\text{CaCl}_2(\text{g})$. Therefore it is concluded that the vapor pressure data are compatible with both bent structures and low bending frequencies (40 to 60 cm^{-1}) for $\text{SrCl}_2(\text{g})$ and $\text{BaCl}_2(\text{g})$.

III. Effect of Temperature on the Mass Spectrum of $\text{BF}_3(\text{g})$

The mass spectrum of $\text{BF}_3(\text{g})$ was measured at several temperatures from room temperature to around 2000°K. The data are needed for subsequent studies of the lower fluorides of boron. $\text{BF}_3(\text{g})$ from an external gas handling system was allowed to leak into a graphite-lined Knudsen effusion cell in the mass spectrometer. At each temperature the intensities of the ions BF_3^+ , BF_2^+ , BF^+ , and B^+ were measured with the shutter slit in both the open and closed positions and the difference current taken as the contribution due to gas molecules in the molecular beam.

Analysis of the results is not yet complete. Considerable uncertainty in the intensity measurements exists because of a very low signal-to-noise ratio, the signal being the molecular beam intensity and noise the signal due to background gas. This problem is encountered frequently in high temperature mass spectrometry.

At present, our instrument is being modified for use of beam chopping techniques which will improve the signal-to-noise ratio for permanent gases by several orders of magnitude. In addition, much useful information concerning the identities of neutral precursors of observed ions will be gotten from the phase angle relationships between the ac intensities of the various ions in a mass spectrum.

IV. Major Accomplishments

New data on the heat of sublimation of boron and on the molecular constants of some gaseous dihalides were obtained, and work has been initiated on modifications to the mass spectrometer which will greatly increase the usefulness of the instrument for high-temperature studies.

V. Problems Encountered

No major technical problems were encountered.

VI. Future Plans

Much of the effort for the next quarter will be devoted to modifying the mass spectrometer for beam chopping. Additional work on some gaseous dihalides will be done, and an ultra-high vacuum system will be constructed for vaporization studies on zirconium and other substances which are reactive towards residual gases at 10^{-6} mm pressure.

VIII. Action Required by Government

None

REFERENCES

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AF 49(638)-1397

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QUARTERLY FINANCIAL REPORT
FOR THE QUARTER ENDING JUNE 30, 1964

	During the Period	To Date
Technical Man-Months of Effort	<u>4.2</u>	<u>4.2</u>
Direct Labor Dollars	\$ 5,508	\$ 5,508
Material Commitments	555	555
Other Direct	152	152
Indirect Costs	<u>6,169</u>	<u>6,169</u>
Total Expenditures	\$ <u>12,384</u>	\$ 12,384
Estimated Expenditures Necessary to Complete the Program		<u>141,913</u>
Total Contract Estimated Cost		<u>\$154,297</u>