AD-A050 602 SRI INTERNATIONAL MENLO PARK CA F/G 11/6

THERMOCHEMISTRY OF GASEOUS COMPOUNDS OF METALS.(U)

JAN 78 D L HILDENBRAND, P D KLEINSCHMIDT F44620-73-C-0037

UNCLASSIFIED AFOSR-78-0163 NL

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AFOSR-TR- 78-0163

January 1978

Final Report

Covering the Period
December 5, 1972 to December 4, 1977

THERMOCHEMISTRY OF GASEOUS COMPOUNDS OF METALS

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Contract F-44620-73-C-0037

SRI International Project No. 2445

Prepared for:

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER AFOSR-78-0163	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) THERMOCHEMISTRY OF GASEOUS COMPOUNDS OF METALS.	5. TYPE OF REPORT & PERIOD COVERED FINAL rept. 5 Dec 72 - 4 Dec 77
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) D. L. HILDENBRAND, P. D. KLEINSCHMIDT, K. H. LAU	8. CONTRACT OR GRANT NUMBER(s) F44620-73-C-0037
9. PERFORMING ORGANIZATION NAME AND ADDRESS SRI INTERNATIONAL 333 RAVENSWOOD AVE MENLO PARK, CA 94025	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2308B1 61102F 2308 B1
11. CONTROLLING OFFICE NAME AND ADDRESS AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA BLDG 410 BOLLING AIR FORCE BASE, D C 20332	12. REPORT DATE Jan 78
	13. NUMBER OF PAGES 14 18p.
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Thermochemistry	**Electron affinities**	**Molybdenum fluorides**
Enthalpies of formation	**High temperature chemistry**	**Alkaline earth halides**
Dissociation energies	**Mass spectrometry**	**Lanthanide fluorides**
Ionization potentials	**Tungsten fluorides**	**Scandium fluorides**

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

The results obtained during a five-year program of thermochemical studies of gaseous inorganic metal compounds are summarized in this report. Thermochemical data were derived from equilibrium measurements made by high-temperature mass spectrometry and related effusion techniques, and from electron impact threshold measurements. Derived thermochemical properties included standard heats of formation, bond dissociation energies, ionization potentials, and in some cases, electron affinities. In studies of the refractory metal fluorides related to chemical corrosion phenomena, the gaseous spacies CF, WF, WF_2, WF_3, WF_4, WF_5, WSF_3, WFS_2, WS_2F_2, MoF, MoF_2, MoF_3, MoF_4, and

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MOF_5 were observed and characterized thermochemically. Estimated spectroscopic and molecular constants of the tungsten and molybdenum fluoride species were found to be consistent with the equilibrium data. Studies of the gaseous diatomic and triatomic bromides and iodides of Ca, Sr, and Ba were completed during the period, and the results were correlated with earlier data for the fluorides and chlorides to estimate the missing dissociation energies of the Be and Mg bromides and iodides. Data for the IIA metal halides are now essentially complete. Systematic studies of the lanthanide and scandium-group compounds were undertaken and, thus far, extensive equilibrium measurements have been completed for EuF, EuF_2, SmO, SmF, SmF_2, SmF_3, ScF, ScF_2, and ScF_3. A comparison of the thermochemical data obtained from this program with values derived from chemiluminescent (CL) reaction studies indicates some discrepancies, and suggests the presence of certain systematic errors in the CL work. The application of the Rittner electrostatic model for calculation of thermochemical properties has been explored in detail, and the strengths and weaknesses of the model have been assessed by comparing calculated values with many of the experimental results from the program. Collectively, the results give a strong insight into the nature of the chemical bonding in these gaseous metal compounds.

Key Words (Concluded)

Carbon monofluoride

Samarium monoxide

Abstract

The results obtained during a five-year program of thermochemical studies of gaseous inorganic metal compounds are summarized in this report. Thermochemical data were derived from equilibrium measurements made by high-temperature mass spectrometry and related effusion techniques, and from electron impact threshold measurements. Derived thermochemical properties included standard heats of formation, bond dissociation energies, ionization potentials, and, in some cases, electron affinities. In studies of the refractory metal fluorides related to chemical corrosion phenomena, the gaseous species CF, WF, WF_2, WF_3, WF_4, WF_5, WSF_3, WSF_2, WS_2F_2 MoF, MoF_2, MoF_3, MoF_4, and MoF_5 were observed and characterized thermochemically. Estimated spectroscopic and molecular constants of the tungsten and molybdenum fluoride species were found to be consistent with the equilibrium data. Studies of the gaseous diatomic and triatomic bromides and iodides of Ca, Sr, and Ba were completed during the period, and the results were correlated with earlier data for the fluorides and chlorides to estimate the missing dissociation energies of the Be and Mg bromides and iodides. Data for the IIA metal halides are now essentially complete. Systematic studies of the lanthanide and scandium-group compounds were undertaken and, thus far, extensive equilibrium measurements have been completed for EuF, EuF_2, SmO, SmF, SmF_2, SmF_3, ScF, ScF_2, and ScF_3. A comparison of the thermochemical data obtained from this program with values derived from chemiluminescent (CL) reaction studies indicates some discrepancies, and suggests the presence of certain systematic errors in the CL work. The application of the Rittner electrostatic model for calculation of thermochemical properties has been explored in detail, and the strengths and weaknesses of the model have been assessed by comparing calculated values with many of the experimental results from the program. Collectively, the results give a strong insight into the nature of the chemical bonding in these gaseous metal compounds.

Introduction

This report summarizes the results obtained from an experimental program concerned with the thermochemistry of gaseous metal compounds, and covers research carried out during the period December 1972 through December 1975. Thermochemical properties are used by the scientist and engineer in evaluating the energetics of chemical reactions, in predicting the direction of spontaneous chemical change, and in calculating the properties of chemical systems at equilibrium. In many instances, however, the thermochemical properties of chemical species of interest in specific applications are not known and cannot be estimated with sufficient accuracy. Our detailed knowledge of chemical bonding has not advanced to the stage that would permit us to evaluate thermochemical properties from purely theoretical considerations. It is necessary, therefore, to obtain the requisite data from new experimental determinations.

The program described here is primarily concerned with determination of the dissociation energies and heats of formation of gaseous metal compounds of interest to aerospace technology. In particular, the studies are relevant to the chemical corrosion and stability of structural materials, and to the development of electronic transition lasers. The elucidation of gas-solid corrosion mechanisms and the application of quasi-equilibrium models requires thermochemical information on the potential corrosion products,[1,2] while similar information is needed in evaluating the energetics of chemical pumping steps in proposed lasing processes.[3]

Although the refractory metals and their alloys are used extensively as structural components in corrosive high-temperature environments containing halogens, very little useful information about the thermochemical properties of the corresponding gaseous metal halides was available prior to the present work. In response to that need, initial phases of the program were devoted to studies of the gaseous lower fluorides of tungsten and molybdenum. These studies yielded standard heats of formation, bond dissociation energies, ionization potentials, and estimated molecular constants of the gaseous fluoride species. Information about negative ion processes involving the tungsten and molybdenum fluorides was also obtained. As a by-product of the W-F studies, new and more accurate thermochemical data were determined for gaseous carbon monofluoride.

Relevant to the chemical laser development and materials compatibility programs, we have studied the thermochemistry of a number of the alkaline earth, scandium-group, and lanthanide gaseous metal compounds, chiefly the halides. Particular emphasis was placed on the determination of accurate dissociation energies for the metal monohalides, since a number of these molecular species have been studied by other techniques such as the beam-gas chemiluminescent (CL) reaction method, sometimes with conflicting results. The results of the present program have aided the interpretation of the CL studies, and have been instrumental in identifying sources of systematic error in dissociation energy determinations made by the CL method, e.g., the effects of small populations of excited electronic states in the metal oven beams on the observed CL emission. Another aspect of the work that has been emphasized is the determination of reaction enthalpies from precise and accurate second-law slope measurements. This is particularly important for the lanthanide and scandium-group halide molecules since the electronic partition functions and the related thermodynamic functions used in third law calculations are highly uncertain. The evaluation of reliable second law entropies, in fact, allows one to estimate the effective electronic contribution to the thermodynamic functions of many of the species being studied, a feature that is useful from both a practical and a theoretical viewpoint. Considerable attention also has been devoted to the application of models for correlating and extending the measured thermochemical data. In particular, the utility of the Rittner electrostatic model for calculation of binding energies has been explored in detail, and the potential for predicting thermochemical data has been assessed. Models of this type are extremely useful in systematizing the properties of families of compounds, and lead to data of much greater reliability than would result from a completely random approach.

A summary of the results obtained on the various chemical systems is given in the third section of this report. Only brief abstracts are included for those studies that have been published in scientific journals.

Experimental

Most of the thermochemical determinations were carried out by means of high temperature mass spectrometry, using an apparatus and experimental technique that has been described previously.[4,5] The spectrometer is a 60° sector, 12-inch radius direction-focusing instrument equipped with a heated Knudsen cell beam source and a Nier-Type electron impact ion source. In essence, the spectrometer is used to sample a collision-free molecular beam emerging from an isothermal effusion oven, and beam composition data obtained from the observed ion abundances are used to derive equilibrium constants and reaction thermochemistry. The data are subjected to several tests to insure that chemical equilibrium is indeed attained in the effusion oven source. In some instances, thermochemical data are also derived from the threshold energies of dissociative ionization processes. The mass spectrometric approach is particularly well suited to these studies of complex high temperature systems because of the selectivity and sensitivity of the method.

Additionally, the torsion-effusion method is used for studies of the thermodynamics of vaporization of various metal compounds. These data can be combined with available thermodynamic data for the condensed phases to yield corresponding information for the gaseous molecules, and are used in conjunction with the mass spectrometric determinations. With this apparatus, effusion recoil force and weight loss are measured simultaneously, so that both pressure and vapor molecular weight can be determined for each experimental point. A detailed description of the torsion apparatus is given in the literature.[6,7]

Summary of Results

a. Carbon Monofluoride

The gaseous equilibrium $S + CF_2 = SF + CF$ was studied over the temperature range 1851 to 2232 K by mass spectrometry, and the derived enthalpy change was used to evaluate the heat of formation of CF $\Delta Hf^\circ_{298} = 58.0 \pm 2.4$ kcal/mol (2.52 ± 0.10 eV), and the dissociation energy $D^\circ_0(CF) = 130.8 \pm 2.4$ kcal/mol (5.67 ± 0.10 eV). The new thermochemical data indicate a slightly higher stability for CF than earlier determinations. Direct measurement by electron impact yielded a value of 9.17 ± 0.10 eV for the vertical ionization potential of CF, in agreement with an indirect result obtained from the photodissociative ionization of C_2F_4.

b. Tungsten Fluorides

Equilibrium and electron impact techniques, both employing mass spectrometry, were used to study the gaseous tungsten fluorides WF_2, WF_3, WF_4, and WF_5. The molecular species were generated by the reaction of both WF_6 and SF_6 with tungsten in an effusion cell at 1000 to 2200 K under demonstrable equilibrium conditions. Reaction enthalpies were derived from second-law analysis of various gaseous equilibria and from electron impact threshold measurements, yielding the standard heats of formation, ΔHf°_{298}, of WF_2 (-20.6 ± 3.2 kcal/mol); WF_3 (-121.2 ± 2.8 kcal/mol); WF_4 (-222.0 ± 2.5 kcal/mol); and WF_5 (-309.1 ± 2.0 kcal/mol). A lower limit of 92 kcal/mol was obtained for the standard heat of formation of WF. Information about molecular ionization potentials is available from the threshold appearance potentials. Thermochemical data were also obtained for gaseous WSF_3, WSF_2, and WS_2F_2.

c. Tungsten Fluoride Negative Ions

Dissociative electron capture processes involving WF_6, WOF_4, and WF_5 were studied by electron impact mass spectrometry and the measured energy thresholds for formation of WF_5^-, WF_4^-, WOF_3^- were used to estimate the electron affinities of the corresponding neutral species as ≥ 0.4, ≥ 1.0, and ≥ 0.3 eV, respectively. The ion WF_4^- was observed as a product from all three reactants and the derived electron affinities of WF_4 from each process are in close agreement, indicating that product excitation is probably negligible in those processes. The results are compared with data obtained from other negative ion studies made by electron impact and collisional ionization techniques.

d. Molybdenum Fluorides

Equilibria among the gaseous molybdenum fluorides were studied by high temperature mass spectrometry, and the results were used to derive thermochemical heats of formation and bond dissociation energies for the gaseous species MoF, MoF_2, MoF_3, MoF_4, MoF_5. Effusion beams containing the gaseous fluorides were generated by the reaction of SF_6 or MoF_6 with elemental Mo at temperatures of 1100-2200 K, and the thermochemical results were derived from a second-law analysis of the equilibrium data. Values of the standard heats of formation, ΔHf°_{298}, obtained are as follows: for MoF, 65.0 ± 2.2 kcal/mol; MoF_2, -40.2 ± 2.9 kcal/mol; MoF_3, -141.5 ± 3.5 kcal/mol; MoF_4, -228.0 ± 3.9 kcal/mol; and MoF_5, -296.7 ± 8.6 kcal/mol. The value for MoF yields the dissociation energy D°_0(MoF) = 110.3 ± 2.2 kcal/mol (4.78 ± 0.10 eV). Estimated spectroscopic and molecular constants are consistent with the gaseous equilibrium data, indicating that assumptions about the derivation of equilibrium constants from ion currents are reasonable.

e. IIA Metal Monobromides

High temperature gaseous equilibria involving CaBr, SrBr, BaBr, and BaCl were studied by mass spectrometry, and the derived heats of reaction were used to evaluate the dissociation energies of the monohalides. The derived values, measured by reference to D°_0(AlBr) and D°_0(AlCl), are D°_0(CaBr) = 73.4 ± 2.2 kcal/mol; D°_0(SrBr) = 78.7 ± 2.2 kcal/mol; D°_0(BaBr) = 85.5 ± 2.2 kcal/mol; and D°_0(BaCl) = 103.3 ± 2.0 kcal/mol. These values are in good agreement with results of recent flame equilibrium determinations, and with semitheoretical values calculated from both the Rittner polarizable-ion model and ionicity-corrected Birge-Sponer extrapolations. On the contrary, values of D°_0 derived from chemiluminescent metal oxidation reactions are rather higher than those obtained by any of the other methods.

f. IIA Metal Monoiodides

Equilibrium effusion beams containing the gaseous molecules CaI, SrI and BaI were generated by the reaction of HI with the corresponding metal oxides at 1500 to 1900 K. Beam composition data obtained by mass spectrometry were used to determine the equilibrium constants of gaseous reactions involving the monoiodides and certain reference molecules.

Reaction enthalpies then were evaluated by second and third law methods, from which the dissociation energies $D_0^\circ(CaI) = 62.1 \pm 2.5$ kcal/mol, $D_0^\circ(SrI) = 63.6 \pm 1.4$ kcal/mol, and $D_0^\circ(BaI) = 71.4 \pm 1.0$ kcal/mol were derived. The results are consistent with data obtained earlier for the diatomic metal fluorides, chlorides and bromides, and they are compatible with the predictions of the Rittner polarizable-ion model. A correlation of the thermochemical properties across the entire halide series allows one to estimate reliable dissociation energies for BeBr, BeI, MgBr and MgI.

g. IIA Metal Dibromides and Diiodides

The vapor pressures of $CaBr_2$, $SrBr_2$, $BaBr_2$, CaI_2, SrI_2, and BaI_2 have been measured by the torsion effusion method. Measurements on $CaBr_2$ and $BaBr_2$ covered both solid and liquid ranges, and those for CaI_2 covered the solid phase only; the remainder were made on the liquid phases. No previous data have been reported for any of the solid dibromides or diiodides, although Peterson and Hutchison[8] have reported vapor pressures for the liquid phases, obtained from effusion weight loss measurements. On the whole, our measurements were made at considerably lower temperatures than those of Peterson and Hutchison,[8] but our extrapolated vapor pressures agree quite well with the weight loss data. The comparison does indicate, however, that the second law slopes of the weight loss data[8] for $SrBr_2$ and BaI_2 are somewhat in error. A third law analysis of the torsion vapor pressure data, using the selected thermodynamic functions given in the JANAF Tables,[9] yields the following standard heats of sublimation in kcal/mol at 298 K: $CaBr_2$ (71.8); $SrBr_2$ (74.6); $BaBr_2$ (79.9); CaI_2 (66.4); SrI_2 (68.8); and BaI_2 (72.6). These values are within a few tenths of a kcal/mol of the selected JANAF Table values based on the vaporization data of Peterson and Hutchison,[8] and, therefore, provide strong support for the estimated molecular constants of the gaseous dihalides. An even more reliable set of thermodynamic functions could be developed by adjusting the bending vibrational frequencies of the gaseous dihalides to be consistent with the combined sets of vapor pressure data.

h. Samarium Monoxide

Because of conflicting results for the dissociation energies (D_0°) of SmO and EuO determined by several different techniques, D_0°(SmO) was redetermined by reference to AlO, TiO, and EuO by means of high temperature mass spectrometry. Derived results for D_0°(SmO) from the exchange reactions with AlO, TiO, and EuO were 135.1, 136.3, and 136.9 kcal/mol, respectively, leading to the selected value 136.0 ± 2 kcal/mol. Extensive equilibrium measurements on the gaseous reaction Al + SmO = AlO + Sm with both pulse counting and dc electrometer techniques gave close agreement between second and third law enthalpies, signifying the estimated thermodynamic function of SmO to be reliable. The new results differ substantially from previously reported data for the reaction Eu + SmO = EuO + Sm, and thereby resolve puzzling discrepancies between the dissociation energies of SmO and EuO.

i. Lanthanide Fluorides

Gaseous equilibria involving the lower fluorides of europium and samarium were studied over wide temperature ranges so that accurate reaction enthalpies could be derived by the second law slope method. The second law approach is necessary because of large uncertainties over the electronic partition functions of the gaseous lanthanide compounds. In both cases, equilibrium was approached by fluorination of the lanthanide oxide, as well as by reduction of the lanthanide trifluoride, with close internal agreement among the derived thermochemical results. The latter is a good indication of equilibrium behavior. A summary of the reaction equilibria studied and the derived results is given in Table I. The dissociation energy of EuF derived from this work is consistent with previously reported values[10,11] of 126 ± 4 and ≥ 130 ± 2 kcal/mol, while that of SmF is somewhat higher than the earlier values[10,11] of 127 ± 4 and ≥ 124 ± 2 kcal/mol. The difluorides have not been studied previously. There appears to be little variation among the individual bond dissociation energies of the Eu and Sm fluorides. If subsequent work shows this pattern to be characteristic of the lanthanide halides, then the estimation of reliable thermochemical properties for the entire lanthanide halide series will be greatly simplified.

j. Scandium Fluorides

Extensive second law studies of reaction equilibria involving the scandium fluorides have also been carried out by mass spectrometry. Effusion oven beams were generated by the reduction of a mixture of ScF_3 and BaF_2 by elemental Zr. In Table II are summarized the reaction equilibria studied, together with the derived results. In contrast to the relative constancy of the individual bond dissociation energies in the Eu and Sm fluorides, those of the Sc fluorides show a substantial variation. The least certain value is $D_0(F_2Sc\text{-}F)$, since the absence of a stable ScF_3^+ parent ion necessitates the use of ScF_2^+ at two different ionizing energies as a measure of ScF_2 and ScF_3. It is planned to check $D_0(F_2Sc\text{-}F)$ by electron impact measurements. Significantly, a comparison of second and third law calculations for the gaseous reaction Sc + BaF = ScF + Ba, for which all molecular parameters are known precisely save for the electronic states of ScF, shows that the low lying $^3\Delta$ state of ScF must be less than 1000 cm^{-1} above ground. The value of $D_0^\circ(ScF)$ derived from this work is lower than the value $D_0^\circ(ScF)$ = 142 ± 3 kcal/mol taken from the measurements of Zmbov and Margrave,[12] while the corresponding results for $D(FSc\text{-}F)$ and $D(F_2Sc\text{-}F)$ are somewhat higher than those reported by Zmbov and Margrave.[12] The sum of the three bond dissociation energies, 446 kcal/mol, is in fair agreement with the heat of atomization of 443 kcal/mol calculated from the NBS data on $ScF_3(g)$.[13] Although the data for $ScF_3(g)$ need further corroboration, the results for ScF and ScF_2 are felt to be essentially complete.

k. Model Calculations of Thermochemical Properties

Two semiempirical models that have proved useful in estimating the thermochemical properties of gaseous halides are the Rittner electrostatic model and the ionicity-corrected Birge-Sponer extrapolation. These two models, their limitations, and their areas of applicability have been reviewed so that their potential utility in estimating missing thermochemical data can be assessed realistically. A comparison of results for the gaseous IIA metal mono- and dihalides, where thermochemical and molecular constant data are relatively complete, shows that the electrostatic model yields dissociation energies with an accuracy of 10 kcal/mol or better. Application of the electrostatic model to the scandium-group and lanthanide halides appears promising, but missing information on equilibrium internuclear distances renders some of the calculations quite uncertain. There is also considerable uncertainty about the nature of the overlap repulsion contribution for the polyatomic halides, but an empirically selected repulsion parameter seems to give satisfactory results. For diatomic molecules, the application of an ionicity correction to the linear Birge-Sponer value generally yields dissociation energies which are accurate to within ten percent or better, but the results are sensitive to the quality of the spectroscopic constants used in the evaluation. When used properly, the two models can be very helpful in providing reliable estimates of thermochemical properties.

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Table I

THERMOCHEMISTRY OF LANTHANIDE FLUORIDES

Reaction	Range, K	ΔH_T kcal/mol	Derived Result kcal/mol
$Eu + CaF = EuF + Ca$	1878-2014	-2.7 ± 2.2	$D_0^\circ(EuF) = 129$
	1618-1785	-3.6 ± 0.9	
$EuF + CaF = EuF_2 + Ca$	1824-2014	-2.5 ± 1.7	$D_0(FEu\text{-}F) = 128$
$Sm + CaF = SmF + Ca$	1730-2334	-8.2 ± 0.6	$D_0^\circ(SmF) = 134$
$SmF + CaF = SmF_2 + Ca$	1448-1643	-6.6 ± 1.3	$D_0(FSm\text{-}F) = 133$
$SmF + SmF_3 = 2SmF_2$	1510-1675	-5.5 ± 1.7	$D_0(F_2Sm\text{-}F) = 128$

Table II

THERMOCHEMISTRY OF THE SCANDIUM FLUORIDES

Reaction	Range, K	ΔH_T kcal/mol	Derived Result kcal/mol
$Sc + BaF = ScF + Ba$	1945-2207	1.5 ± 1.0	$D_0^\circ(ScF) = 136$
$Sc + ScF_2 = 2ScF$	1945-2207	8.4 ± 0.7	$D_0(FSc\text{-}F) = 145$
$ScF + ScF_3 = 2ScF_2$	1945-2175	20.0 ± 2.0	$D_0(F_2Sc\text{-}F) = 165$