AD-A248 651

2

PL-TR-91-2280

THERMOCHEMISTRY OF ATMOSPHERIC METAL REACTIONS

K. H. Lau
D. L. Hildenbrand

SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

DTIC
ELECTE
MAR 10 1992
S B D

November 1991

Final Report
10 May 1990-31 December 1991

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

PHILLIPS LABORATORY
AIR FORCE SYSTEMS COMMAND
HANSCOM AIR FORCE BASE, MASSACHUSETTS 01731-5000

92-06119

This technical report has been reviewed and is approved for publication.

Terry L. Thiem
(Signature)
TERRY L. THIEM, Capt., USAF
Contract Manager

Charles P. Pike
(Signature)
CHARLES P. PIKE
Branch Chief

This document has been reviewed by the ESD Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS).

Qualified requestors may obtain additional copies from the Defense Technical Information Center. All others should apply to the National Technical Information Service.

If your address has changed, or if you wish to be removed from the mailing list, or if the addressee is no longer employed by your organization, please notify PI/TSI, Hanscom AFB, MA 01731-5000. This will assist us in maintaining a current mailing list.

Do not return copies of this report unless contractual obligations or notices on a specific document requires that it be returned.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response including the time for reviewing instructions searching existing data sources gathering and maintaining the data needed and completing and reviewing the collection of information Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports 1215 Jefferson Davis Highway Suite 1204 Arlington VA 22202 4302 and to the Office of Management and Budget, Paperwork Reduction Project (0704 0188), Washington DC 20503

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
November 1991

3. REPORT TYPE AND DATES COVERED
Final Report(10 May 1990-31 Dec 1991)

4. TITLE AND SUBTITLE
Thermochemistry of Atmospheric Metal Reactions

5. FUNDING NUMBERS
PE 62101F
PR 7601
TA 30
WU CM
Contract F19628-90-K-0030

6. AUTHOR(S)
K. H. Lau
D. L. Hildenbrand

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

8 PERFORMING ORGANIZATION REPORT NUMBER
1165

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Phillips Laboratory
Hanscom AFB, MA 01731-5000

Contract Manager: Edmond Murad/WSSI

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
PL-TR-91-2280

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

As part of a research program carried out during the period May, 1990 through September 1991, we have used effusion-beam mass spectrometry to study the thermochemistry and related aspects of several chemical systems pertinent to the understanding of some atmospheric metal reactions. First, the Na_2O-CO_2-H_2O system was examined for evidence of gaseous $NaHCO_3$ or other carbonates that may be important as sinks for sodium in the atmosphere. Second, the mass spectrum and ionization efficiency curves of Na_2O vapor were studied to obtain information about the thermodynamic stability of the superoxide NaO_2. And thirdly, the thermochemical properties of the gaseous oxides OsO_2 and OsO were determined to supplement earlier work on OsO_3. The results are summarized in three journal preprints.

14 SUBJECT TERMS
Sodium carbonates, Sodium oxides, Osmium Oxides, Thermochemistry, Mass spectrometry

15 NUMBER OF PAGES
48

16 PRICE CODE

17 SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19 SECURITY CLASSIFICATION OF ABSTRACT**	**20 LIMITATION OF ABSTRACT**
Unclassified	Unclassified	Unclassified	SAR

CONTENTS

MASS SPECTROMETRIC SEARCHE[illegible] GASEOUS SODIUM CARBONATES

MASS SPECTRUM AND SUBLIMATION PRESSURE OF SODIUM OXIDE VAPOR; STABILITY OF THE MOLECULE NaO$_2$

THERMOCHEMISTRY OF THE GASEOUS OSMIUM OXIDES

COPY INSPECTED 6

Accession For
NTIS GRA&I ☑
DTIC TAB ☐
Unannounced ☐
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or Special
A-1

SUMMARY

This report summarizes the results of a research program associated with the chemistry of atmospheric metal reactions and with contamination of spacecraft environment in low earth orbit. It was initiated in response to a Broad Agency Announcement from the Air Force Geophysics Laboratory, and was conducted during the period May 1990 through September 1991. Three topics were investigated, (1) the thermodynamic stability of gaseous sodium bicarbonate and carbonate; (2) the stability and the bond energy of the gaseous sodium dioxide molecule, NaO_2; and (3) the thermochemical properties of the gaseous osmium oxides. The research results are detailed in three manuscripts appended to this report.

RESULTS

The background, the experimental techniques used, and the derived results from this research are described in the three manuscripts attached to the report.

1. The manuscript "Mass spectrometric searches for gaseous sodium carbonates" has been accepted for publication in the Journal of Physical Chemistry and is currently in press.

2. The manuscript "Mass spectrum and sublimation pressure of sodium oxide vapor; stability of the molecule NaO_2 contains all research results on this topic obtained under the AFGL sponsored program. It will later be combined with additional work sponsored by the Electric Power Research Institute into a composite manuscript for submission to the Journal of Chemical Physics.

3. The manuscript "Thermochemistry of the gaseous osmium oxides" has been submitted for publication in the Journal of Physical Chemistry.

ACKNOWLEDGMENT

We wish to express our thanks to Drs. E. Murad, L. Watson, and R. Dressler, and to 1Lt T. Thiem of Phillips Laboratory for stimulating discussions in the course of this work.

MASS SPECTROMETRIC SEARCHES FOR GASEOUS SODIUM CARBONATES

D.L. Hildenbrand and K.H. Lau
SRI International, Menlo Park, CA 94025

ABSTRACT

In connection with modeling of the chemistry of meteor-deposited sodium in the upper atmosphere, we have examined the mass spectra of several pertinent sodium-containing effusion sources for evidence of gaseous $NaHCO_3$, Na_2CO_3, or any other Na-C-O-H species. Although clear and unambiguous evidence for the presence of $Na_2CO_3(g)$ was obtained with various sources involving solid and liquid Na_2CO_3 and NaOH in the presence of gaseous CO_2, H_2O and H_2, all searches for $NaHCO_3(g)$ were negative. An upper limit of about 29 ± 5 kcal mol^{-1} was estimated for the bond strength $D(NaOH\text{-}CO_2)$, based on the detection limit for $NaHCO_3$ and measured abundances of NaOH and CO_2. Preliminary thermodynamic quantities were derived for $Na_2CO_3(g)$. The results are discussed in terms of atmospheric chemistry models in the literature.

INTRODUCTION

Gaseous $NaHCO_3$ has been proposed[1] as a possible terminal reaction product for meteor-deposited sodium in the upper atmosphere, and also as a potential source of "sudden sodium layers" in the E region of the ionosphere by means of the dissociative attachment process

$$NaHCO_3 + e \rightarrow Na + HCO_3^- \qquad (1)$$

which is expected to be efficient.[2] Beams of HCO_3^- have been generated by the interaction of O^- and OH^- with CO_2-H_2O mixtures,[3,4] but the electron affinity and related thermochemical properties have not been established experimentally. To our knowledge nothing is known about the gaseous species $NaHCO_3$.

The rate constants for the gaseous reaction $NaOH + CO_2 + M$, in which $NaHCO_3$ is the expected gaseous product, were reported,[5] but no evidence regarding product identity was presented. And for HCO_3^-, the geometrical structure parameters and binding energy of the gaseous ion were calculated from molecular theory,[6] but there has been no experimental confirmation. We are not aware of any other observations on gaseous bicarbonates.

To gain more information about these species, we have examined the mass spectra of vapors emitted from an effusion cell source containing Na_2CO_3 or NaOH in the presence of CO_2, H_2O and H_2. Pressures of the added gases were increased to maximum permissible levels to optimize conditions for $NaHCO_3$ formation. The results of these experiments are described below.

EXPERIMENTAL

All parts of the tubular effusion cell source were fabricated from platinum. The main part of the cell was a 0.99 cm ID thin-walled tube with an internal 0.32 cm diam tube for gas addition; the tube cap contained a 0.11 cm diam effusion orifice. A schematic of the cell and heater arrangement is shown in Figure 1. The Na_2CO_3 samples were contained in a Pt cup in the hot zone of the cell, as in a normal effusion experiment with gas addition. With NaOH, which has a higher vapor pressure, the sample was supported on a Pt screen below the heater zone. A ball of Pt wire placed in the sample region was effective at the higher temperatures in confining the molten samples by surface tension. Another ball of Pt wire placed near the exit orifice served as a baffle to increase gas-surface collisions and to promote equilibration. The reactive gases could be added singly or in pre-mixed combinations.

Mass spectra were obtained with the magnetic-sector instrument and experimental technique described in previous publications.[7,8] As always, observed ion signals were checked for response to displacement of the neutral beam-defining slit to ascertain their effusion cell origin. The cell configuration is expected to yield an essentially equilibrium distribution of species. A pressure calibration based on the established vapor pressure of gold was combined with estimated ionization cross section ratios to evaluate species partial pressures from measured ion intensities.

The Na_2CO_3 powder and NaOH pellet samples were reagent grade materials used without further purification. CO_2 and H_2 reagent gases were obtained from the Matheson Co., while laboratory distilled water was used as the source of H_2O.

RESULTS

A. Na_2CO_3 Reactions

Initial experiments on the vaporization of Na_2CO_3 in the absence of added gases showed emission of detectable quantities of gaseous Na, CO_2 and O_2 above 800 K, indicating the principal vaporization process to be

$$Na_2CO_3(s) = 2\ Na(g) + CO_2(g) + 1/2\ O_2(g) \qquad (2)$$

Above 1050 K, smaller parent ion signals corresponding to the species Na_2CO_3, NaO, Na_2O, and an NaOH impurity that depleted with time were also observed. The threshold appearance potential of $Na_2CO_3^+$ was 7.5 ± 0.3 eV, while those of NaO^+ and Na_2O^+ agreed with values found previously in the sublimation of $Na_2O(s)$.[9] The $Na_2CO_3^+$ signal was easily detectable, varied reproducibly with temperature, and showed the characteristically-sharp beam profile associated with effusion-beam species. A few $Na_2CO_3^+$ intensity measurements were made over the range 1065 to 1123 K for subsequent thermodynamic analysis.

The addition of CO_2, H_2O and H_2, singly or together, up to pressures approaching the molecular flow limit of 10^{-4} atm yielded no significant changes in the mass spectrum other than the expected increase in the NaOH signal with H_2O and H_2. In particular, the $NaHCO_3^+$ mass position at m/e 84 was scanned carefully, but no signal above the background count rate of a few ions per second could be detected. Likewise, there was no evidence for any new fragment ions such as $NaCO_3^+$, $NaHCO_2^+$ or $NaCO_2^+$. $NaOH^+$ is a potential fragment from $NaHCO_3$, but an abundant parent ion contribution precludes that possibility.

The negative ion spectrum was also scanned at the high flows of H_2O and CO_2 in order to check for the presence of HCO_3^- that could result from dissociative electron attachment to $NaHCO_3$, reaction (1). However, no detectable HCO_3^- signal was observed under any of the experimental conditions. A moderate O^- signal with a maximum intensity at an electron energy of about 8 eV was observed, probably as a result of dissociative attachment to CO_2.[10]

In all, the search gave no evidence for the presence of $NaHCO_3$.

B. NaOH Reactions

In order to increase the partial pressure of NaOH and optimize the conditions for $NaHCO_3$ formation, the direct vaporization of NaOH in the presence of CO_2 was examined. At about 1150 K, partial pressures of NaOH and CO_2 approaching 10^{-4} atm were obtained. Again, however, no parent or fragment ion species associated with $NaHCO_3$ were detected under any conditions. A search of the negative ion spectrum gave no evidence for HCO_3^- or any related species, other than O^-.

With CO_2 addition, the parent ion $Na_2CO_3^+$ was detected readily at a level of about 10^5 smaller than $NaOH^+$ and CO_2^+, showing that the technique has ample sensitivity for detection of minor Na-containing species.

C. Preliminary Thermodynamic Analysis

Although the search for evidence of $NaHCO_3$ yielded only negative results, one can use the instrumental detection limit to set an upper bound on the $NaHCO_3$ partial pressure and use this information to derive a limiting value for the standard enthalpy of formation. NaOH and CO_2 partial pressures in the effusion source were evaluated from the measured parent ion intensities and were coupled with upper bound values for $NaHCO_3$ to estimate a lower limit to the equilibrium constant of the reaction

$$NaHCO_3(g) = NaOH(g) + CO_2(g) \qquad (3)$$

for subsequent thermodynamic analysis. The points selected were those with the highest partial pressures of NaOH and CO_2, since these conditions put the most stringent limits on the stability of $NaHCO_3$. A conservative estimate of the $NaHCO_3$ partial pressure was derived by increasing the minimum detectable $NaHCO_3^+$ signal limit (~1 ion/sec) by a factor of five, to allow for possible undetected fragmentation.

From two measurements at 1165 K, with NaOH, CO_2 and $NaHCO_3$ partial pressures of 3×10^{-5}, 7×10^{-5} and $< 8 \times 10^{-11}$ atm, respectively, one calculates for reaction (3) an equilibrium constant $K° > 26$ atm. A third law calculation with estimated thermal functions for $NaHCO_3$ and established functions for NaOH and CO_2 then yields the limiting enthalpy change $\Delta H°_{298}(3) < 29$ kcal mol^{-1}, with an estimated uncertainty of 5 kcal mol^{-1} based on a possible error of a factor of 5 in $K°$ and an uncertainty of 3 cal K^{-1} mol^{-1} in the Gibbs energy functions. The origins of the thermal functions used in the calculation are described in the Appendix. Note that $\Delta H°_{298}(3)$ is equivalent to the bond dissociation energy $D(NaOH\text{-}CO_2) < 29 \pm 5$ kcal mol^{-1}.

From measured intensities of the $Na_2CO_3^+$ signal, the equilibrium pressure of the sublimation process

$$Na_2CO_3(s) = Na_2CO_3(g) \qquad (4)$$

was estimated at seven temperatures over the range 1065 to 1123 K. Since the ion yield curve of Na_2O^+ indicated a probable fragmentation contribution from Na_2CO_3, a correction was applied to the $Na_2CO_3^+$ intensities to account for this effect in third law calculations. Measurements were restricted to the region below the melting point of Na_2CO_3 to avoid difficulties created by creep of the liquid carbonate out of the sample container. The equilibrium pressures and derived thermodynamic data are given in Table I, leading to the average value for the enthalpy of sublimation of Na_2CO_3 at 298 K of 96.0 ± 3 kcal mol^{-1}. This value for $\Delta H°_{298}(\text{sub})$ and the established properties of the solid then yield the standard enthalpy of formation $\Delta_f H°_{298}(Na_2CO_3,g) = -174.2 \pm 3$ kcal mol^{-1}.

An independent value for $Na_2CO_3(g)$ can be derived from the gaseous equilibrium

$$Na_2O(g) + CO_2(g) = Na_2CO_3(g) \qquad (5)$$

with the results summarized in Table I. From the equilibrium data for reaction (5), we derive $\Delta H°_{298}(5) = -75.8 \pm 3$ kcal mol^{-1} and $\Delta_f H°_{298}(Na_2CO_3,g) = -173.8 \pm 4$ kcal mol^{-1}, in good agreement with the value from the sublimation reaction. To our knowledge, there are no reported values for comparison.

We would not expect to observe any gaseous HCO_3 or H_2CO_3 under our experimental conditions, even with H_2 and CO_2 pressures near 10^{-4} atm. Assuming even a large exothermicity for the reaction

$$H_2O(g) + CO_2(g) = H_2CO_3(g) \qquad (6)$$

similar to that for H_2SO_4 formation from H_2O and SO_3, a third law calculation with estimated thermal functions shows that H_2CO_3 would be several orders of magnitude below the detection limit. The same applies to HCO_3. Therefore, the results yield no useful information about H_2CO_3 or HCO_3.

DISCUSSION

In view of the stability and ready detectability of $Na_2CO_3^+$ one would tend to expect similar stability for the parent ion $NaHCO_3^+$. Both neutrals are closed-shell species, probably ($Na^+ CO_3^= Na^+$) and ($Na^+ HCO_3^-$), and loss of a single electron should lead to a stable parent ion, as found for the alkali sulfates, chromates, molybdates and nitrates.[11] In any event, the lack of a detectable parent or fragment ion is ascribed to the relatively low thermodynamic stability of $NaHCO_3(g)$ and the consequent low equilibrium partial pressure.

Interestingly enough, the limiting bond dissociation energy $D(NaOH\text{-}CO_2) < 29 \pm 5$ kcal mol^{-1} derived from this work is compatible with the value of 30 ± 5 kcal mol^{-1} adopted by Ager and Howard[5] from a consideration of several estimates for $D(OH^- \text{-} CO_2)$. Although obviously not definitive, our results provide at least an upper bound on the stability of $NaHCO_3$ and indicate that the high estimates[4,6] for $D(OH^- \text{-}CO_2)$ ranging from 56 to 88 kcal mol^{-1} may be in error. In the proposed stratospheric reaction scheme of Murad and Swider,[1] the reaction

$$NaOH + CO_2 + M \rightarrow NaHCO_3 + M$$

would have an exothermicity < 29 kcal mol^{-1} or < 1.2 eV. Although this exothermicity limit is felt to be reliable, it should be remembered that $NaHCO_3$ could be present at significant levels under the non-equilibrium conditions prevailing in the upper atmosphere and in some of the laboratory experiments.[5]

The derived value for the enthalpy of sublimation of Na_2CO_3 at 298 K, 96.0 ± 3 kcal mol^{-1}, is significantly higher than tabulated[12] values for K_2CO_3 and Cs_2CO_3, 81.2 and 78.5 kcal mol^{-1}, respectively, both ± 5 kcal mol^{-1}. It is also higher than the corresponding value[13] for Na_2SO_4, 87.0 kcal mol^{-1}.

Since our search proved negative, we can say nothing about the thermochemistry of the negative ion HCO_3^- or about the energetics of reaction (1). The species $H_2CO_3(g)$ has recently been identified[14] as a product of the decomposition of $NH_4HCO_3(s)$ at 400 K, but as noted above, equilibrium calculations indicate that this species should be completely negligible under our experimental conditions.

APPENDIX

Thermodynamic data for Na_2CO_3(s), H_2O(g), and CO_2(g) were taken from the JANAF Tables,[15] while values for NaOH(g) and Na_2O(g) were taken from the compilation of Glushko et al.[12] Thermal functions for $NaHCO_3$(g) and Na_2CO_3(g) were calculated from molecular constants estimated as follows.

Na_2CO_3(g)

The moments of inertia were estimated from corresponding values in Na_2SO_4, K_2CO_3 and K_2SO_4,[12] while the fundamental frequencies were selected by analogy with those tabulated for K_2CO_3.[12]

$NaHCO_3$(g)

A planar structure was assumed, with structural parameters for the HCO_3 group as given by the calculations of Jonsson et al.;[6] the Na-O distance was taken to be 0.23 nm, with the Na located along an Na-C-O-H axis. The COONa frequencies were taken from those estimated above for Na_2CO_3, while those for the COH group were estimated by analogy with those of LiOH and NaOH.[12] The estimated frequencies associated with the overall -HCO_3 group are consistent with the HCO_3^- fundamentals assigned from the infrared spectra of decomposed bicarbonate salts in alkali halide matrices.[16]

A summary of the estimated molecular constants of Na_2CO_3 and $NaHCO_3$ are listed in Table II in terms of the moments of inertia (I), fundamental frequencies (ω), rotational symmetry number (σ) and electronic ground state statistical weight (g). Tables of thermal functions calculated from these constants are given in Tables III and IV, based on a standard state pressure of 1 atm. Uncertainties in the entropies and Gibbs energy functions are estimated to be on the order of 2 cal K^{-1} mol^{-1} at 298 K and 3 cal K^{-1} mol^{-1} at 1000 K. For the sake of internal consistency, more significant figures are included than are warranted by the accuracy of the calculated functions.

ACKNOWLEDGMENT

This work was supported by the Phillips Laboratory, Air Force Systems Command, Hanscom AFB, MA.. We are grateful for stimulating discussions with Dr. E. Murad of that organization.

REFERENCES

1. Murad, E. ; Swider, W. Geophys. Res. Lett. **1979**, 6, 929.
2. von Zahn, U.; Murad, E. Geophys. Res. Lett. **1990**, 17, 147.
3. Keesee, R. G.; Lee, N.; Castleman, A. W.,Jr. J. Am. Chem. Soc., **1979**, 101, 2599.
4. Hierl, P. M.; Paulson, J. F. J. Chem. Phys. **1984**, 80, 4890.
5. Ager, J. W.,III; Howard, C. J. J. Geophys. Res. **1987**, 92, 6675.
6. Jonsson, B. G.; Karlstrom, G.; Wennerstrom, H. J. Am. Chem. Soc. **1978**, 100, 1658.
7. Hildenbrand, D. L. J. Chem. Phys., **1968**, 48, 3657; **1970**, 52, 5751.
8. Kleinschmidt, P. D.; Lau, K. H.; Hildenbrand, D. L. J. Chem. Phys. **1981**, 74, 653.
9. Hildenbrand, D. L.; Murad, E. J. Chem. Phys. **1970**, 53, 3403.
10. Krauss, K. Z. Naturforsch. **1961**, A 16, 1378.
11. Levin, R. D.; Lias, S. G. Nat. Bur. Stand. Rept. **1982** NSRDS-NBS 71.
12. Glushko, V. P.; Gurvich, L. V.; Bergman, G. A.; Veitz, I. V.; Medvedev, V. A.; Kachkuruzov, G. A.; Yungman, V. S. Thermodynamic Properties of Individual Substances, Vol. IV, Academy of Sciences, Moscow, USSR, 1982.
13. Lau, K. H.; Brittain, R. D.; Lamoreaux, R. H.; Hildenbrand, D. L. J. Electrochem. Soc. **1985**, 132, 3041.
14. Terlouw, J. K.; Lebrilla, C. B.; Schwarz, H. Angew. Chem. Int. Ed. Engl., **1987**, 26, 354.
15. Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. J. Phys. Chem. Ref. Data, **1985**, 14, Suppl. No. 1.
16. Bemitt. D. L.; Hanman, K. O.; Hisatsune, I. C. J. Chem. Phys. **1965**, 42, 3553.

TABLE I

Equilibrium Data and Derived Thermochemistry for Reactions Involving $Na_2CO_3(g)$

$Na_2CO_3(s) = Na_2CO_3(g)$

T/K	$P \times 10^{10}$ atm	ΔH°_{298} kcal mol^{-1}	$\Delta_f H^\circ_{298}(Na_2CO_3,g)$ kcal mol^{-1}
1065	0.60	95.4	-174.9
1093	1.5	95.6	-174.7
1108	2.6	95.7	-174.6
1121	4.1	95.7	-174.6
1121	3.0	96.4	-173.9
1121	2.1	97.2	-173.1
1123	3.4	96.3	-174.0

$Na_2O(g) + CO_2(g) = Na_2CO_3(g)$

T/K	$K^\circ \times 10^5$ atm^{-1}	ΔH°_{298} kcal mol^{-1}	$\Delta_f H^\circ_{298}(Na_2CO_3,g)$ kcal mol^{-1}
1287	1.5	-75.7	-173.5
1298	1.0	-75.1	-173.1
1352	0.6	-76.7	-174.7

TABLE II

Estimated Molecular Constants of $NaHCO_3$ and Na_2CO_3

Molecule	$I_xI_yI_z$ $g^3\,cm^6$	σ	$g_\circ$	ω_i, cm^{-1}
$NaHCO_3$	6×10^{-114}	1	1	1450, 1400, 1050, 880, 720, 700, 280, 240, 60, 3600, 600, 450
Na_2CO_3	4×10^{-113}	2	1	1450, 1050, 880, 720, 280(2), 240(2), 170, 1400, 700, 60

TABLE III

ESTIMATED THERMODYNAMIC FUNCTIONS OF GASEOUS Na_2CO_3

$H^\circ_{298} - H^\circ_0 = 4.651$ cal·mol^{-1}

T (K)	Cp (cal·K^{-1}·mol^{-1})	S° (cal·K^{-1}·mol^{-1})	$-[G^\circ_T - H^\circ_{298}]/T$ (cal·K^{-1}·mol^{-1})	$H^\circ_T - H^\circ_{298}$ (cal·mol^{-1})
298	21.450	81.901	81.901	0
300	21.499	82.034	81.901	40
400	23.841	88.554	82.774	2312
500	25.621	94.075	84.496	4789
600	26.945	98.869	86.501	7421
700	27.925	103.100	88.576	10167
800	28.657	106.879	90.632	12998
900	29.211	110.288	92.630	15892
1000	29.637	113.388	94.553	18835
1100	29.970	116.229	96.396	21816
1200	30.233	118.849	98.159	24827
1300	30.445	121.277	99.845	27861
1400	30.618	123.540	101.458	30915
1500	30.760	125.657	103.001	33984
1600	30.878	127.646	104.480	37066
1700	30.978	129.522	105.899	40159
1800	31.062	131.295	107.261	43261
1900	31.134	132.976	108.570	46371
2000	31.196	134.575	109.831	49488
2100	31.250	136.098	111.046	52610
2200	31.297	137.553	112.218	55737
2300	31.338	138.945	113.350	58869
2400	31.374	140.280	114.444	62005
2500	31.407	141.561	115.503	65144
2600	31.435	142.793	116.530	68286
2700	31.461	143.980	117.524	71431
2800	31.484	145.125	118.490	74578
2900	31.505	146.230	119.427	77728
3000	31.523	147.298	120.339	80879

TABLE IV

ESTIMATED THERMODYNAMIC FUNCTIONS OF GASEOUS $NaHCO_3$

$H^\circ_{298} - H^\circ_0 = 3.941\ cal\cdot mol^{-1}$

T **(K)**	**Cp** **($cal\cdot K^{-1}\cdot mol^{-1}$)**	**S°** **($cal\cdot K^{-1}\cdot mol^{-1}$)**	**$-[G^\circ_T - H^\circ_{298}]/T$** **($cal\cdot K^{-1}\cdot mol^{-1}$)**	**$H^\circ_T - H^\circ_{298}$** **($cal\cdot mol^{-1}$)**
298	18.474	74.679	74.679	0
300	18.530	74.793	74.679	34
400	21.192	80.506	75.440	2026
500	23.178	85.460	76.960	4250
600	24.646	89.822	78.747	6645
700	25.749	93.708	80.612	9167
800	26.599	97.204	82.471	11786
900	27.274	100.377	84.287	14481
1000	27.823	103.280	86.043	17237
1100	28.278	105.954	87.733	20042
1200	28.662	108.431	89.356	22890
1300	28.989	110.739	90.913	25773
1400	29.270	112.897	92.407	28686
1500	29.513	114.925	93.842	31625
1600	29.725	116.837	95.220	34588
1700	29.910	118.645	96.545	37570
1800	30.073	120.359	97.821	40569
1900	30.217	121.989	99.050	43583
2000	30.344	123.542	100.236	46612
2100	30.458	125.025	101.382	49652
2200	30.559	126.445	102.489	52703
2300	30.649	127.805	103.560	55763
2400	30.731	129.111	104.598	58832
2500	30.804	130.367	105.604	61909
2600	30.870	131.577	106.579	64993
2700	30.931	132.743	107.527	68083
2800	30.985	133.869	108.448	71179
2900	31.035	134.957	109.343	74280
3000	31.080	136.010	110.215	77386

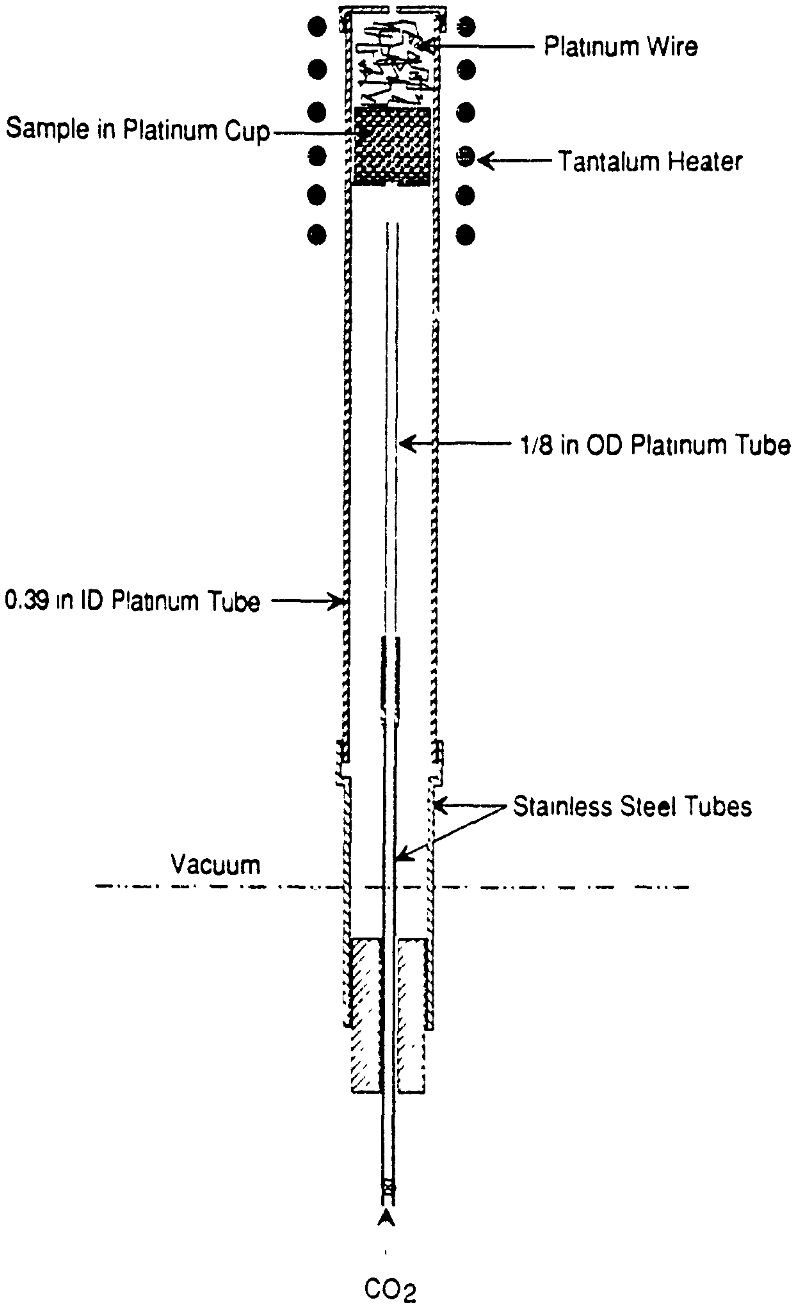

Figure 1. Schematic diagram of the platinum knudsen cell arrangement.

MASS SPECTRUM AND SUBLIMATION PRESSURE OF SODIUM OXIDE VAPOR; STABILITY OF THE MOLECULE NaO_2

D.L. Hildenbrand and K.H. Lau
SRI International, Menlo Park, CA 94025

INTRODUCTION

The thermochemical properties of the gaseous oxides of sodium are of importance in the analysis of atmospheric reactions of meteor-deposited sodium, and in assessing the transport of trace-element sodium in coal combustion streams. However, there are some conflicting interpretations of the Na-O vapor chemistry that need to be resolved before reliable models of the reaction chemistry can be developed.

In 1984, Lamoreaux and Hildenbrand[1] reviewed the thermochemical literature on alkali oxides, selected best values of these quantities, and used the results to evaluate equilibrium partial pressures of various species over the oxide phases under neutral, reducing and oxidizing conditions over wide temperature ranges. For the Na-O system, the results[1] were based primarily on a mass spectrometric study[2] of $Na_2O(c)$ sublimation that showed the major sublimation process to be

$$Na_2O(c) = 2\ Na(g) + 0.5\ O_2(g) \qquad (1)$$

with minor amounts of the gaseous oxides NaO and Na_2O also present. Although not mentioned explicitly, the mass spectrometric studies[2] gave no evidence for the presence of the gaseous dioxide NaO_2 that had been postulated as a stable species from photometric studies of sodium-containing flames.[3] From the mass spectrometric detection limit for the parent ion NaO_2^+, an upper limit of 115 kJ mol^{-1} was estimated for the bond dissociation energy $D_0(Na\text{-}O_2)$.[1] As will be shown, the much higher flame[3] value of $D_0(Na\text{-}O_2) = 272 \pm 12$ kJ mol^{-1} (later revised[4] to 234 ± 12 kJ mol^{-1}) implies that NaO_2 should be a major species in the equilibrium vapor over $Na_2O(c)$.

Between 1983 and the present, there followed a number of kinetic and beam studies in which the presence of NaO_2 was inferred but not confirmed, and values of $D_0(Na\text{-}O_2)$ were estimated from the results. Figger et al.[5] studied the chemiluminescent reaction of alkali dimers with O_2 by a crossed-beam technique and evaluated $M\text{-}O_2$ bond strengths from the cut-off wavelengths; no chemiluminescence was observed with Na, but $D_0(Na\text{-}O_2) < 184$ kJ mol^{-1} was estimated. Hynes et al.[6] made a more complete study of sodium reactions in $H_2/O_2/N_2$ flames, and estimated $D_0(Na\text{-}O_2) = 163 \pm 21$ kJ mol^{-1} from a detailed kinetic modeling of the results. Somewhat later, Plane et al.[7] studied the kinetics of the gas phase reaction $Na + O_2 + N_2$ and recommended $D_0(Na\text{-}O_2) = 202$ kJ mol^{-1}; theoretical calculations with several different basis sets indicated $D_0(Na\text{-}O_2) = 184$ kJ mol^{-1}, but are not considered definitive. Yet another kinetic study of the reaction $Na + O_2 + N_2$ at somewhat higher temperatures was interpreted to yield a lower limit of 230 ± 5 kJ mol^{-1} for $D_0(Na\text{-}O_2)$.[8] And just recently, Steinberg and Schofield[9] have come up with a revised interpretation of the flame modeling data pushing $D_0(Na\text{-}O_2)$ up to 243 ± 8 kJ mol^{-1}; to our knowledge, however, the background and reasoning in support of this major new revision have not been published, and only the value itself has been stated. In each of these studies, the identity of the NaO_2 gaseous reaction product was inferred from the reaction order or some other indirect measure, rather than from a direct spectroscopic observation of this species.

The way in which $D_0(Na\text{-}O_2)$ affects the Na-O gas-phase chemistry can be illustrated from thermodynamic calculations of the equilibrium composition of the vapor over $Na_2O(c)$. From the established thermodynamic properties of $Na_2O(c)$ and gaseous Na, O_2, Na_2O and NaO, reviewed and compiled by Glushko et al.,[10] calculations show that Na_2O and NaO are at least several orders of magnitude less abundant than Na and

O_2, and will have no effect on gross properties such as the total sublimation pressure. By assuming a vapor composed of Na, O_2 and NaO_2, one can calculate partial and total sublimation pressures of $Na_2O(c)$ for various values of $D_0(Na\text{-}O_2)$ and the related standard enthalpy of formation; NaO_2 thermal functions used in the calculations were evaluated from sources described in the Appendix. The calculation was done for the established condition of congruent sublimation and for a temperature of 1000 K, which is in the measurable effusion-pressure regime; composition is relatively independent of temperature in this regime.

As shown in Figure 1, NaO_2 is a relatively minor species with no significant influence on the sublimation behavior for $D_0(Na\text{-}O_2)$ less than about 190 kJ mol^{-1}. For larger values of $D_0(Na\text{-}O_2)$, NaO_2 becomes increasingly important, and at $D_0(Na\text{-}O_2)$ = 243 kJ mol^{-1}, the value recommended by Steinberg and Schofield,[9] NaO_2 is a major species, replacing O_2. The overall vaporization process would then be

$$2\ Na_2O(c) = 3\ Na(g) + NaO_2(g) \qquad (2)$$

with the O_2 partial pressure reduced by a factor of 25. More significantly, a value of 243 kJ mol^{-1} would force the total sublimation pressure to increase by a factor of 2.4, from 7.06×10^{-7} atm to 1.27×10^{-6} atm, above the calculated pressure for a system composed of Na and O_2.

Such major effects on the sublimation behavior of Na_2O can be checked experimentally in several different ways. First, the total sublimation pressure of $Na_2O(c)$ can be measured with an accuracy of about 10 %. It will then be possible to distinguish between the low stability of NaO_2 dictated by reaction (1), for which the total pressure can be calculated accurately from established thermochemical data, and the much higher stability postulated by Steinberg and Schofield[9] that leads to a substantially higher pressure via reaction (2).

Additionally, Steinberg and Schofield[9] have suggested that, despite its proposed presence as a major species, NaO_2 perhaps was not detected in the earlier mass spectrometric studies[2] of Na_2O sublimation because the parent ion NaO_2^+ may not have been stable and could have dissociated to Na + O_2^+ or Na^+ + O_2 before reaching the ion collector. It should be noted that there is no direct evidence to support this assumption. Fragmentation processes involving rupture of the O-O bond in NaO_2 were ruled out[9] because of the relatively high stability of that bond relative to the Na-O bond and the low level of NaO^+ observed. The possibility of NaO_2 fragmentation was not examined in the earlier studies,[2] but it can be checked from detailed measurements of the ionization efficiency (IE) curves of O_2^+ and Na^+ in Na_2O vapor, and comparison with similar curves obtained from pure O_2 and atomic Na. The presence of a major species must be manifested in one of the fragment ions; it cannot escape detection.

The objective of the work reported here was to determine the sublimation pressure of Na_2O by the torsion-effusion method, and to re-examine the mass spectrum of Na_2O vapor and the IE curves of O_2^+ and Na^+ for evidence bearing on the partial pressure and thermodynamic stability of gaseous NaO_2.

EXPERIMENTAL

The torsion-effusion apparatus and related experimental technique have been described in a previous publication and references cited therein.[11] Pt-Rh alloy effusion cells and caps of the type described earlier[12,13] were used in this work. The cell was heated by a non-inductively wound electric furnace surrounding the fused silica vacuum enclosure, and temperature was measured with a Pt, Pt-Rh thermocouple. Frequent checks with vapor pressure standards have shown the measured pressures to be accurate within 10 % or better. Basically, the torsion system is an effusion manometer with which total pressure can be determined from the measured angular deflection, and from the mechanical and geometrical constants of the system. If mass loss is measured simultaneously, the average molecular weight of effusing vapor can also be determined, generally with an accuracy of about 10 %.

Mass spectrometric measurements were made with the same basic instrument used in the earlier work on Na_2O sublimation,[2] which is described in the literature.[14,15] This is a 30.5 cm radius, magnetic-sector instrument equipped with an effusion cell source. Many significant improvements have been made to the original instrument,[14,15] including the addition of a high-capacity cryopump to the ion source region that facilitates accurate measurements on non-condensable beam species such as O_2. As always, measured signals were checked for response to displacement of the molecular beam-defining slit to eliminate possible background contributions. Ionization threshold energies were evaluated by the vanishing current method, using atomic Na and background H_2O as standards.

In the mass spectrometric studies, the sodium oxide sample was held in a conventional single-chamber platinum effusion cell with 0.15 cm diam orifice. Cell temperature was measured with a Pt, Pt-Rh thermocouple firmly attached to the cylindrical surface of the cell with a Pt band. A few measurements of the ionization efficiency of atomic sodium were also made, using elemental Na contained in a high-density graphite effusion cell.

Although satisfactory samples of crystalline Na_2O were available from commercial sources in past studies,[2,16] no suppliers could be located in the course of the present work. Instead, $Na_2O(c)$ was prepared by decomposition of sodium peroxide, $Na_2O_2(c)$, in situ. For the mass spectrometric studies, which were completed first, a 93 % sodium peroxide sample obtained from Fluka Chemical Corp. was loaded into a conventional Pt effusion cell and the decomposition monitored by following the O_2^+ parent ion signal. Initially, the O_2^+ effusion-cell signal was strong and steady in the 650 to 700 K region, but after a number of hours, the signal depleted to an immeasurably low value, indicating the disappearance of the Na_2O_2 phase. No other species were observed until about 950 to 1000 K, when Na, Na_2O, NaO, and O_2, appeared along with the impurity species K, NaOH and $Na_2(OH)_2$. The hydroxide peaks were particularly strong, but after several hours at 1100 K, the K and Na-O-H peaks dropped to negligible levels. Measurements of the mass spectrum and the Na^+ and O_2^+ ionization efficiency curves were initiated at this point.

For the torsion-effusion pressure measurements, a 97 % sample of Na_2O_2(c) obtained from CERAC was first purified by heating to 700 K in a stream of O_2 to remove water and other volatile impurities, while supressing dissociation. The peroxide sample was then loaded into the torsion cell and heated slowly into the 600 to 700 K range, where the O_2 dissociation pressure was measured and decomposition to Na_2O(c) was monitored. When the pressure became undetectably small at 700 K, the temperature was increased until steady pressures were obtained at 1000 to 1050 K.

RESULTS

A. Mass Spectrometric Measurements

After disappearance of the peroxide phase, and the K and Na-O-H impurities, the relative intensities of Na^+, O_2^+, NaO^+ and Na_2O^+ matched reasonably well those reported earlier for Na_2O sublimation.[2] At 1100 K, the intensity ratios Na^+(10 eV)/O_2^+(17 eV)/Na_2O^+(10 eV)/NaO^+(11 eV) were 290/16/0.05/0.06, within a factor of two or better of values[2] obtained more than twenty years ago with the same instrument but under slightly different instrumental conditions. Repeated searches for parent NaO_2^+ at 1100 K were negative, despite the very low instrument background at 55 amu.

Furthermore, the IE curves of Na^+ and O_2^+, with threshold energies of 5.0 and 12.0 eV, both ± 0.2 eV, gave no evidence for fragment ion formation from NaO_2, as suggested by Steinberg and Schofield.[9] The observed thresholds are in good agreement with the spectroscopic ionization potentials of Na at 5.14 eV and O_2 at 12.08 eV. There seems to be a misunderstanding[9] that non-monoenergetic electron impact thresholds are likely to have inaccuracies of 1 to 2 eV; however, ample evidence has been obtained over the years to show that our ion source design and technique routinely yield thresholds with accuracies of 0.1 to 0.3 eV.[15] Plots of the normalized IE curves of Na^+ and O_2^+ from Na_2O vapor compared to corresponding curves from atomic Na and background O_2 at room temperature are shown in Figures 2 and 3. For both Na^+ and O_2^+, the curves from Na_2O vapor are indistinguishable from those of pure O_2 and atomic Na, showing that there is no discernible evidence whatever for any fragment ion contributions from NaO_2 by the processes

$$NaO_2 + e \rightarrow Na^+ + O_2 + 2e \qquad (3)$$

and

$$NaO_2 + e \rightarrow Na + O_2^+ + 2e \qquad (4)$$

which were postulated[9] to appear at about 7.7 eV in the Na^+ curve and 14.6 eV in the O_2^+ curve. The O_2^+ beam signal from $Na_2O(c)$ was more than 95 % of the total signal, showing that the instrument background contribution was almost negligible; nevertheless, the small background portion was subtracted out to give the true effusion-beam signal for plotting the curve. Incidentally, the appearance of structure in the O_2^+ curves is real, and is due to additional thresholds at 16.1, 17.0 and 18.2 eV associated with excited electronic states of O_2^+.[17] In any event, one can conclude with certainty that the observed Na^+ and O_2^+ signals have no sources other than atomic Na and molecular O_2, respectively, and that the speculation by Steinberg and Schofield[9] regarding NaO_2 as a source of these signals is incorrect.

In addition, the ratio of Na^+ intensities at 20 eV ionizing energy to those at 8 eV should give further indication about the possibility of Na^+ formation by reaction (3), since a higher energy fragmentation onset beyond about 8 eV would raise the ion yield and increase the ratio $I(Na^+, 20\ eV)/I(Na^+, 8\ eV)$ with respect to the value in atomic Na. The values of this ratio are 4.5 ± 0.5 and 5.6 ± 0.5 in Na_2O vapor and atomic Na vapor, respectively, showing that the two are essentially the same, thereby offering no evidence of fragmentation from NaO_2 via reaction (3). In contrast, however, the ratio $I(Na^+, 20\ eV)/I(Na^+, 8\ eV)$ is 9.6 ± 0.5 in Na_2SO_4 vapor, where molecular Na_2SO_4 makes up only

37 mol % of the total pressure dominated by the decomposition products Na, SO_2 and O_2,[18] giving clear evidence of the electron impact fragmentation of Na_2SO_4 to Na^+ at energies above about 12 eV. We feel that if NaO_2 were present in Na_2O vapor at the level suggested by Steinberg and Schofield[9] there would have been ample indication in the Na^+ ion ratios and in the Na^+ or O_2^+ IE curves; as discussed above, no such indication was detected.

The significance of these results is that NaO_2 could be at most a relatively minor species in the equilibrium vapor over $Na_2O(c)$. Based on the IE curves and intensity ratios, we estimate an upper limit of 0.01 to 0.05 for the mole fraction of NaO_2, which from Figure 1 corresponds to a firm upper limit of 190 kJ mol^{-1} for $D_0(Na\text{-}O_2)$; this is more than 50 kJ mol^{-1} smaller than the value of 243 kJ mol^{-1} proposed by Steinberg and Schofield,[9] and the true value may be even smaller. At present it is difficult to refine this value further for a species which is present at a mole fraction of 0.01 or less, and which may not form a stable parent ion. If one assumes a stable NaO_2^+ parent ion, the detection limit of about 1×10^{-10} atm at 1100 K leads by way of a third law calculation to an upper limit of about 125 kJ mol^{-1} for $D_0(Na\text{-}O_2)$. Because the possibility of a minor NaO_2 species with an unstable parent ion cannot be excluded, we take a $D_0(Na\text{-}O_2)$ upper limit of 190 kJ mol^{-1} as the principal result of the mass spectroscopic studies reported here.

REFERENCES

1. R.H. Lamoreaux and D.L. Hildenbrand, J. Phys. Chem. Ref. Data **13**, 151 (1984).
2. D.L. Hildenbrand and E. Murad, J. Chem. Phys. **53**, 3404 (1970).
3. M.J. McEwan and L.F. Phillips, Trans. Faraday Soc. **62**, 1717 (1966).
4. G.J. Dougherty, M.J. McEwan and M.J. Phillips, Combust. Flame **21**, 253 (1973).
5. H. Figger, W. Schrepp, and X. Zhu, J. Chem. Phys. **79**, 1320 (1983).
6. A.J. Hynes, M. Steinberg, and K. Schofield, J. Chem. Phys. **80**, 2585 (1984).
7. J.M.C. Plane, B. Rajasekhar, and L. Bartolotti, J. Phys. Chem. **93**, 3141 (1989).
8. P. Marshall, A.S. Narayan, and A. Fontijn, J. Phys. Chem. **94**, 2998 (1990).
9. M. Steinberg and K. Schofield, J. Chem. Phys. 94, 3901 (1991).
10. V.P. Glushko, L.V. Gurvich, G.A. Bergman, I.V. Veitz, V.A. Medvedev, G.A. Kachkuruzov and V.S. Yungman, "Thermodynamic Properties of Individual Substances", Vol. IV, Academy of Sciences, Moscow, USSR (1982).
11. K.H. Lau, D. Cubicciotti, and D.L. Hildenbrand, J. Chem. Phys. **66**, 4532 (1977).
12. K.H. Lau, D. Cubicciotti, and D.L. Hildenbrand, J. Electrochem. Soc. 126, 490 (1979).
13. R.D. Brittain, K.H. Lau, and D.L. Hildenbrand, J. Electrochem. Soc. 134, 2900 (1987).
14. D.L. Hildenbrand, J. Chem. Phys. **48**, 3657 (1968); **52**, 5751 (1970).
15. D.L. Hildenbrand, Int. J. Mass Spectrom. Ion Phys. **4**, 75 (1970); **7**, 255 (1971).
16. P.A.G. O'Hare, J. Chem. Phys. **56**, 4513 (1972).
17. C.E. Brion, J. Chem. Phys. **40**, 2995 (1964).
18. K.H. Lau, R.D. Brittain, R.H. Lamoreaux, and D.L. Hildenbrand, J. Electrochem. Soc. **132**, 3041 (1985).
19.

MASS SPECTRA OF VAPOR OVER $Na_2O(c)$ AT 1100 K

	Relative Intensity	
Ion	(1970) [a]	(1991) [b]
Na^+ (10 eV)	520	290
O_2^+ (17 eV)	17	16
NaO^+ (11 eV)	0.04	0.06
Na_2O^+ (10 eV)	0.09	0.05

a Commercial sample of $Na_2O(c)$

b Sample prepared from $Na_2O_2(c)$

Na^+ Intensity Ratios

Sample	$I(Na^{\pm}, 20\ eV)/I(Na^{\pm}, 8\ eV)$
Na	5.6 Â 0.5
Na_2O	4.5 Â 0.5
Na_2SO_4	9.6 Â 0.5

Vapor over Na_2SO_4 contains about 45 mol % Na, 35 mol % Na_2SO_4

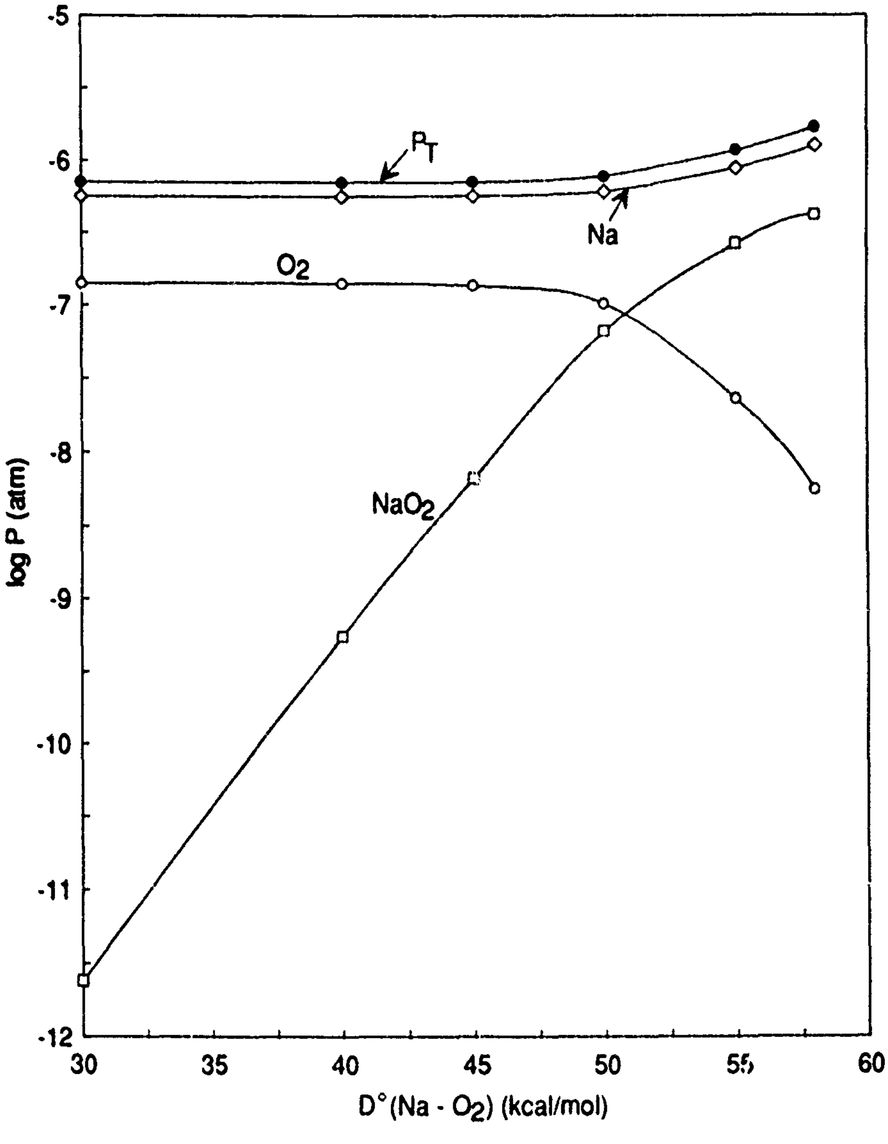

Figure 1 Equilibrium composition of vapor over $Na_2O(c)$ as a function of $D(Na - O_2)$.

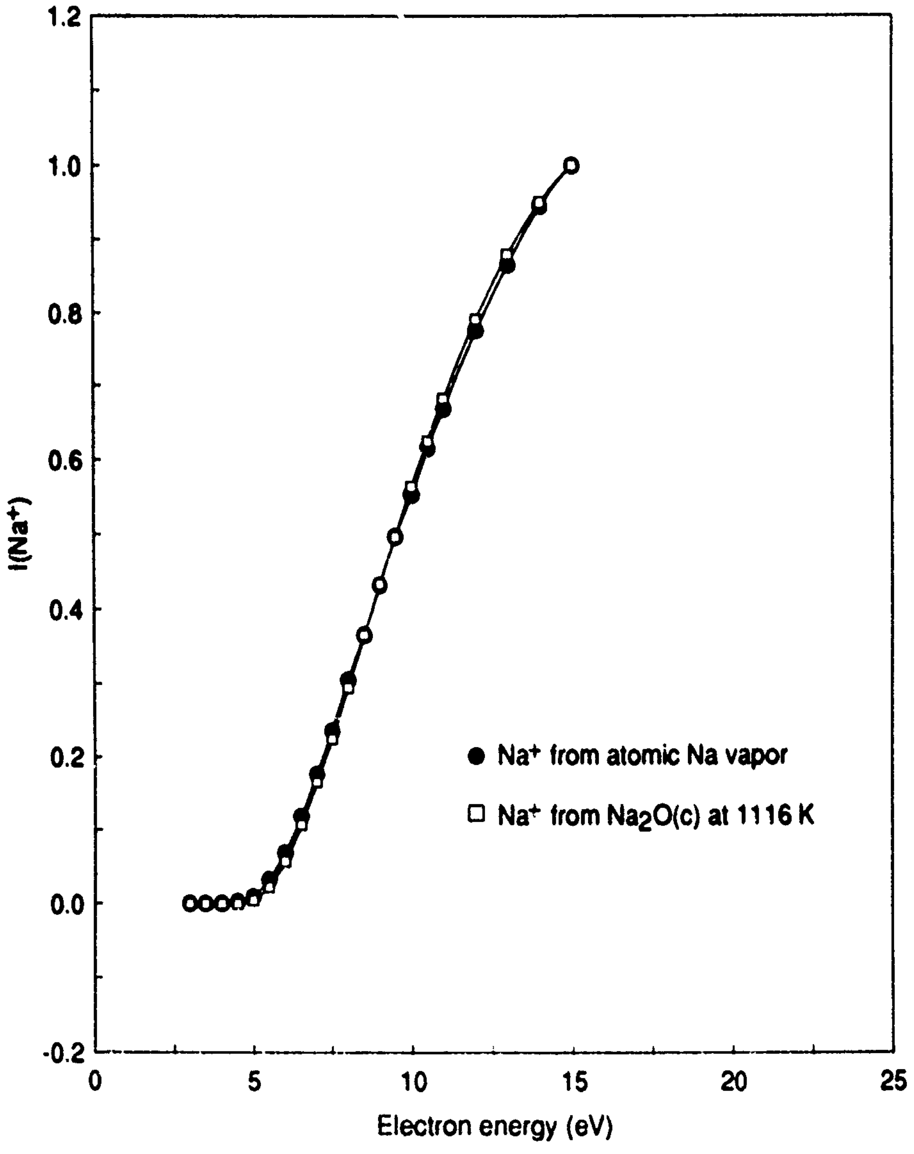

Figure 2. Ionization efficiency curves of Na^+.

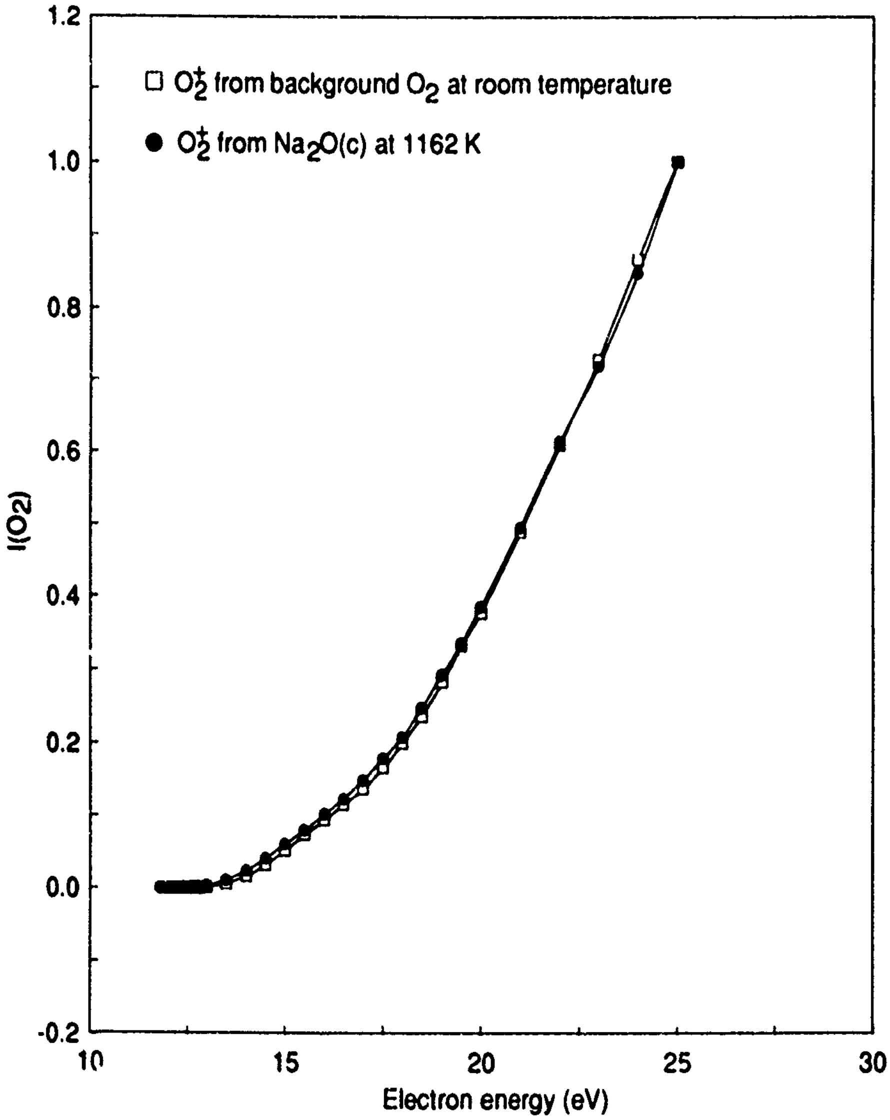

Figure 3. Ionization efficiency curves of O_2^+.

Thermochemistry of the Gaseous Osmium Oxides

D.L. Hildenbrand and K.H. Lau
SRI International, Menlo Park, CA 94025

ABSTRACT

The gaseous osmium oxide species OsO_4, OsO_3, OsO_2, and OsO were generated by reaction of $O_2(g)$ with Os(c) in a heated alumina effusion cell, and thermochemical data were derived from equilibrium measurements made by mass spectrometry. Although OsO_4 and OsO_3 were observed as low as 1000 K, OsO_2 and OsO were detected only at temperatures above 1800 K. From third law analysis of the gaseous reaction equilibria $OsO_4 = OsO_3 + 1/2\ O_2$, $OsO_3 = OsO_2 + O$, and $OsO_2 = OsO + O$, the bond dissociation energies $D(O_3Os\text{-}O)$, $D(O_2Os\text{-}O)$, D(OOs-O), and D(Os-O) were found to be 435, 570, 542, and 575 kJ mol^{-1}, respectively, at 298 K. There are no previous results on OsO_2 and OsO. Results are compared with other information in the literature.

INTRODUCTION

Recent observation of the removal of metallic osmium films by energetic O atoms in low earth orbit[1] has stimulated interest in the thermochemical properties of the gaseous osmium oxides. Following earlier mass spectrometric studies by Grimley et al.[2] of the reaction equilibrium

$$OsO_4(g) = OsO_3(g) + 1/2\ O_2(g) \qquad (1)$$

Watson et al.[3] reinvestigated reaction (1) by the same method and obtained the enthalpy change $\Delta H°_{298}(1) = 176 \pm 29$ kJ mol^{-1}, some 127 kJ mol^{-1} larger than the previous value.[2] Both studies[2,3] reported evidence for the presence of neutral OsO_2 but intensities were too low for thermochemical measurements. Watson et al.[3] reported an upper limit of 12.2 ± 0.4 eV for the ionization potential of OsO_2. Pedley and Marshall[4] estimated the dissociation energy of OsO as 594 ± 84 kJ mol^{-1} by analogy with related oxides, but there have been no direct thermochemical studies of OsO or OsO_2.

We have now completed a brief thermochemical study of the Os-O system, also by mass spectrometry and at somewhat higher temperatures than those attained previously.[2,3] Both OsO_2 and OsO were clearly identified and characterized thermochemically, and the results are reported here.

EXPERIMENTAL

Measurements were made with the magnetic-sector mass spectrometer system and heated effusion-beam source described in previous publications.[5,6] A powdered sample of Os(c) was contained in an alumina effusion cell with alumina gas inlet tube at the base. The cell contained a 0.15 cm diameter effusion orifice, with a length of 0.35 cm. A thin platinum cover was placed over the alumina cell to provide good black body conditions for pyrometer temperature measurement; apertures in the top and side of the Pt cover were aligned with the cell orifice and black body cavity. A few experiments were done with a mixture of Os(c) and TiO_2(c) in a conventional alumina effusion cell.

With the gas inlet cell, the flow of O_2 was controlled reproducibly with an external molecular leak valve. At most temperatures, gas flow rates were varied to check on attainment of chemical equilibrium. All ion signals were checked for response to displacement of the neutral beam-defining slit between effusion cell and ion source to clarify their origin; except for temperatures above 1500 K where some background OsO_4 was observed because of high O_2 flow rates, the Os-O species clearly originated in the effusion cell. Ionization efficiency curves were recorded automatically with an x-y recorder and the threshold behavior interpreted by the vanishing current method.[6]

After ion species were identified from their masses and isotopic spectra, and reliable threshold appearance potentials (AP) were determined, neutral partial pressures and equilibrium constants, K°, were evaluated from parent ion intensities determined a few eV (3 eV in this work) above their respective thresholds to avoid overlapping fragmentation contributions. Partial pressures were derived from the ion intensities using a sensitivity constant determined by calibration with a laboratory vapor pressure standard and the application of a cross section correction.[7] In the Os-O studies, the ionization efficiency curves and mass spectra indicated that no fragmentation corrections were required to obtain an accurate total ion yield for third law calculations. This procedure has been found to be quite reliable, and the resulting K° values are estimated to be accurate within a factor of two.[7,8] All other aspects of the experimental procedure and data interpretation are as described previously.[5,6]

The osmium powder sample of 99.9% purity was obtained from Johnson Matthey, while the O_2(g) and TiO_2(c) were reagent grade materials obtained from commercial suppliers.

RESULTS

With O_2 admitted to the cell containing the Os(c) sample at 1000 to 1500 K, OsO_4^+ and OsO_3^+ were observed with threshold AP's of 12.3 and 11.3 eV, both ± 0.3 eV. A somewhat weaker OsO_2^+ signal with an AP of 15.5 eV was also observed in this range, and is clearly a fragment ion from OsO_3. These values agree well with those reported by Watson et al.[3] and indicate that OsO_4^+ and OsO_3^+ are indeed parent ions under the experimental conditions. Other AP data in the literature for OsO_4 and OsO_3 are discussed by Watson et al.[3]

Above about 1850 K, OsO_2^+ and OsO^+ signals with threshold AP's of 10.2 and 9.5 eV were observed. These AP's are in line with anticipated values for the ionization potentials (IP) of the corresponding neutrals, which would be expected to show increasing Os orbital character as the oxygen ligands are removed successively, and to converge on the IP of atomic Os at 8.7 eV. Therefore, the AP data provide unambiguous evidence for the presence of OsO_2 and OsO in the effusing vapor. Our AP values for OsO_2^+ and OsO^+ are in fair agreement with OsO_2 and OsO IP's of 11.2 and 9.7 eV, respectively, estimated by Dillard and Kiser[9] from electron impact data on OsO_4; they also agree well with measured IP values for RuO_2 and RuO.[9] Not surprisingly, our AP(OsO_2^+) is about 2 eV lower than the upper limit IP(OsO_2) reported by Watson et al.[3], indicating that OsO_2 was not present in detectable amounts in the earlier work. The additional parent ions O_2^+ and O^+ were observed in the effusion beam, with AP's of 12.0 and 13.5 eV, in accord with the known IP's of O_2 and O.

Parent ion intensities measured at 3 eV above the respective thresholds were used together with the pressure calibration constant and estimated cross section ratios to evaluate the equilibrium constants $K°$ for reaction (1) and for the additional reactions

$$OsO_3(g) = OsO_2(g) + O(g) \qquad (2)$$

$$OsO_2(g) = OsO(g) + O(g) \qquad (3)$$

with the results shown in Tables 1 and 2; also shown are third law enthalpies calculated with thermal functions described in the Appendix. $K°$ values were found to be independent of gas flow rate and species partial pressure under these conditions, providing evidence that chemical equilibrium was achieved.

For reaction (1), our values of $K°(1)$ are in close agreement with the selected results obtained by Watson et al.[3] with V_2O_5(s) as oxidizer; their average third law enthalpy yields $K°(1) = 1.9 \times 10^{-3}\ (\text{atm})^{1/2}$ at 1288 K, the same as our average value from Table 1. It is significant that our results are in closer agreement with the data obtained with the V_2O_5 oxidizer (which they considered to be equilibrium data) than with the O_2.[3] In any event, the comparison shows that reproducible results were obtained. Rather than doing a more complete study of reaction (1), our intent here was only to seek corroboration of the work of Watson et al.[3] Our equilibrium data yield the average third law enthalpy change $\Delta H^\circ_{298}(1) = 185 \pm 12$ kJ mol^{-1}, in agreement within the estimated errors with the selected value of Watson et al.[3] 176 ± 29 kJ mol^{-1}, which is an average of second and third law results. It is not clear why the earlier second law results of Grimley et al.[2] gave the much lower value $\Delta H^\circ_{298}(1) = 54$ kJ mol^{-1}, but it clearly should be discarded in favor of the newer results.

It is worth noting that at temperatures above 1500 K, OsO_4 persisted at noticeable background levels in the ion source, despite fast cryopumping there, and the parent ion did not show the normal sharp slit profile characteristic of effusion cell species, as was seen at lower temperatures. This is no doubt due mostly to the relatively high O_2 pressures in the cell (approaching 10^{-4} atm) used to enhance the small OsO_2^+ and OsO^+ signals. All other signal profiles showed normal behavior. As seen in Table 1, the equilibrium measurements on OsO_4 were made at 1013 and 1288 K.

Equilibrium data and derived results for reactions (2) and (3) are shown in Table 2. In order to obtain workable parent ion intensities of OsO_2^+ and OsO^+ at AP + 3 eV ionizing energy, it was necessary to push O_2 pressures in the cell to near 10^{-4} atm. At 2052 K, the ratio of parent ion intensities $OsO_3^+/OsO_2^+/OsO^+/O^+$ was 281/2.8/1/291. Several data points for reaction (2) obtained with the Os(c) + TiO_2(c) beam source are in good agreement with those from the Os(c) + O_2(g) source as seen in Table 2, providing further evidence that the results are reproducible equilibrium values. The selected enthalpies are the average third law values $\Delta H^\circ_{298}(2) = 570 \pm 17$ kJ mol^{-1}, and $\Delta H^\circ_{298}(3) = 542 \pm 17$ kJ mol^{-1}. Estimated uncertainties arise from a possible error of a factor of two in K°, and 8 J K^{-1} mol^{-1} in the Gibbs energy functions. Because of the low OsO_2^+ and OsO^+ signal levels and the limited temperature range, second law analysis is considered to be unsuitable.

From the derived enthalpy changes for reactions (1), (2), and (3) and the enthalpy of atomization of OsO_4(g) evaluated from the established enthalpy of formation (see Appendix) and the thermochemical properties of atomic Os and O, we derive the bond dissociation energies at 298 K D(O_3Os-O) = 435, D(O_2Os-O) = 570, D(OOs-O) = 542, and D(Os-O) = 575 kJ mol^{-1}, all ± 20 kJ mol^{-1}. There are no previous literature values on D(O_2Os-O) or D(OOs-O) for comparison. Our value for OsO leads to the dissociation energy $D°_0$(OsO) = 571 ± 20 kJ mol^{-1} (5.92 ± 0.22 eV), which is in accord with the qualitative estimate of Pedley and Marshall[4] of 594 ± 84 kJ mol^{-1}, based solely on the values for related transition metal oxides. As far as is known, there are no experimental thermochemical data for OsO, so that the $D°_0$ value reported here is the first direct measurement. The bond dissociation energies and standard enthalpies of formation, $\Delta_f H°_{298}$, of the Os-O species derived from this work are summarized in Table 3.

DISCUSSION

It is gratifying that our measured equilibrium constants for reaction (1) at 1013 and 1288 K agree closely with those of Watson et al.[3] determined with the Os(c) + V_2O_5(s) system. Although the invariance of K°(1) as P(OsO_4) changed by more than a factor of ten indicates attainment of chemical equilibrium in our Os(c) + O_2(g) measurements, Watson et al.[3] inferred from the lack of agreement between second and third law enthalpies that equilibrium was not reached in their experiments with O_2(g).

Osmium and ruthenium are unique in the formation of stable gaseous tetroxides. The new bond dissociation energy data, listed in Table 4, show that the first three bonds formed as oxygen ligands are added to the central Os atom are of approximately equal strength, varying from only 542 to 575 kJ mol^{-1}. The fourth bond, D(O_3Os-O), is considerably weaker at 435 kJ mol^{-1}, indicating that some type of promotion energy must be required in making the transition from the +6 to the +8 oxidation state of Os. Ruthenium shows the same type of behavior in that D(O_3Ru-O) is about 370 kJ mol^{-1}, while D(O_2Ru-O), D(ORu-O), and D(Ru-O) are 448, 490, and 530 kJ mol^{-1}, respectively.[4,10] The relative weakness of this fourth bond correlates with the chemical instability of the Ru and Os tetroxides, and with the effectiveness of $OsO_4(g)$ as an oxidizing agent. As noted by Dillard and Kiser[9] and also in our own laboratory, RuO_4 and to some extent OsO_4 leave a troublesome electrically-conducting film on ion source components, probably from reaction with metal surfaces to form a conducting deposit of Ru or Os lower oxides.

It is worth noting that among the platinum group metals, which include Ru, Rh, Pd, Os, Ir, and Pt and involve the filling of the second half of the 4d and 5d shells, the strongest metal-oxygen bonds are formed by Os. The dissociation energies of the gaseous monoxides, which are a good indication, fall in the order 571, 523, 410, 402, 385, and 376 kJ mol^{-1} for the monoxides of Os, Ru, Ir, Rh, Pt and Pd, respectively; values for oxides other than OsO were taken from Pedley and Marshall.[4]

ACKNOWLEDGMENT

This work was supported by the Phillips Laboratory, Hanscom Air Force Base, MA. We are indebted to Lyn Watson for calling our attention to the paper on the electronic band spectrum of OsO.

APPENDIX

The thermochemical properties of O and O_2 were taken from the JANAF Thermochemical Tables,[11] while those of atomic Os were taken from Hultgren et al.[12] For calculation of the thermal functions of OsO_3 and OsO_2, the Os-O internuclear distances were estimated to be 0.175 nm, slightly longer than the electron diffraction value of 0.17116 nm found in OsO_4.[13,14] Other parameters for the Os-O species were selected as described below; the selected molecular constants are summarized in Table 4 in terms of the moments of inertia (I), rotational symmetry number (σ), electronic ground state statistical weight (g_0), and vibrational frequencies (ω). Gibbs energy functions calculated with the selected molecular constants are listed in Table 5; the functions are calculated for the ideal gas state at 1 atm pressure.

OsO_4(g)

Spectroscopic constants were taken from the values summarized by McDowell et al.[14] The standard enthalpy of formation listed by Kubaschewski and Alcock[15] was adopted.

OsO_3(g)

A planar structure of D_{3h} symmetry was assumed, along with a $^1\Sigma$ electronic ground state. Following Watson et al.[3] the vibration frequencies were assumed to be the same as those of WO_3 listed in the JANAF Tables.[11]

OsO_2(g)

The molecule was assumed to be linear symmetric, with frequencies similar to those given in the JANAF Tables[11] for MoO_2 and WO_2. Because of the four non-bonding 5d valence electrons, the ground electronic state was assumed to be $^3\Sigma$.

OsO(g)

The adopted rotational constant and vibration frequency were derived from analysis of the electronic spectrum.[16] The electronic ground state was taken to be $^5\Delta$, as with RuO and FeO.[17]

REFERENCES

1. Peters, P. N.; Gregory, J. C.; Swann, J. T. *Appl. Opt.* **1986**, *25*, 1290.

2. Grimley, R. T.; Burns, R. P.; Inghram, M. G. *J. Chem. Phys.* **1960**, *33*, 308.

3. Watson, L. R.; Thiem, T.; Dressler, R. A.; Salter, R. H.; Murad, E. *J. Phys. Chem.* In press.

4. Pedley, J. B.; Marshall, E. M. *J. Phys. Chem. Ref. Data* **1983**, *12*, 967.

5. Hildenbrand, D. L. *J. Chem. Phys.* **1968**, *48*, 3657; **1970**, *52*, 5751.

6. Hildenbrand, D. L. *Int. J. Mass Spectrom. Ion Phys.* **1970**, *4*, 75; **1971**, *7*, 255.

7. Lau, K. H.; Hildenbrand, D. L. *J. Chem. Phys.* **1987**, *86*, 2949.

8. Hildenbrand, D. L.; Lau, K. H.; Russell, T. D.; Zubler, E. G.; Struck, C. W. *J. Electrochem. Soc.* **1990**, *137*, 3275.

9. Dillard, J. G.; Kiser, R. W. *J. Phys. Chem.* **1965**, *69*, 3893.

10. Norman, J. H.; Staley, H. G.; Bell, W. E. *Advances in Chemistry Series 72*, American Chemical Society, Washington, D.C., 1968, p. 101.

11. Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. No. 1.

12. Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelley, K. K.; Wagman, D. D. *Selected Values of the Thermodynamic Properties of the Elements*, American Society of Metals, Cleveland, OH, 1973.

13. Seip, H. M.; Stolevik, R. *Acta Chem. Scand.* **1966**, *20*, 385.

14. McDowell, R. S.; Radziemski, L. J.; Flicker, H.; Galbraith, H. W.; Kennedy, R. C.; Nereson, N. G.; Krohn, B. J.; Aldridge, J. P.; King, J. D. *J. Chem. Phys.* **1978**, *69*, 1513.

15. Kubaschewski, O.; Alcock, C. B. *Metallurgical Thermochemistry*, 5th ed, Pergamon, New York, 1979.

16. Balfour, W. J.; Ram, R. S. *J. Mol. Spectrosc.* **1984**, *105*, 360.

17. Krauss, M.; Stevens, W. J. *J. Chem. Phys.* **1985**, *82*, 5584.

Table 1

Equilbrium Constants and Derived Third Law Enthalpies for the Reaction

$$OsO_4(g) = OsO_3(g) + 1/2\ O_2(g) \qquad (1)$$

T/K	***K*°(1) ($atm^{1/2}$)**		**$\Delta H°_{298}$ kJ mol^{-1}**
1013	3.3×10^{-5}		182.3
1013	3.8×10^{-5}		181.1
1288	1.6×10^{-3}		189.4
1288	2.0×10^{-3}		187.1
1288	2.0×10^{-3}		187.1
		Av.	185.4

Table 2

Equilibrium Constants and Derived Third Law Enthalpies for the Reactions

$$OsO_3(g) = OsO_2(g) + O(g) \qquad (2)$$

$$OsO_2(g) = OsO(g) + O(g) \qquad (3)$$

T/K	***K*°(2)** **(atm)**	**ΔH°$_{298}$(2)** **kJ mol^{-1}**	***K*°(3)** **(atm)**	**ΔH°$_{298}$(3)** **kJ mol^{-1}**
1897	3.0×10^{-9}	574.2		
1965	1.9×10^{-8}	564.8		
1965	1.4×10^{-8}	569.8		
2014	3.9×10^{-8}	566.8	1.6×10^{-6}	537.3
2014	3.8×10^{-8}	567.3	1.6×10^{-6}	537.3
2014	2.6×10^{-8}	573.6	1.2×10^{-6}	542.1
2052	4.3×10^{-8}	574.2	1.9×10^{-6}	544.6
2052	5.4×10^{-8}	572.2	2.7×10^{-6}	538.6
2052	5.0×10^{-8}	573.5	1.9×10^{-6}	544.6
2125	2.8×10^{-7}	563.6	4.1×10^{-6}	550.3
	Av.	570.0	Av.	542.1
2006 [a]	3.2×10^{-8}	568.1		
2059 [a]	4.6×10^{-8}	576.9		

[a] From $Os(c) + TiO_2(c)$ system; all others $Os(c) + O_2(g)$ system

Table 3

Derived Thermochemcial Data

Gaseous Species	**$\Delta_f H^\circ_{298}$ kJ mol^{-1}**	**Bond**	**D°_{298} kJ mol^{-1}**
OsO_4	-336.4 ± 8	(O_3Os-O)	435
OsO_3	-151.0 ± 21	(O_2Os-O)	570
OsO_2	169.4 ± 21	(OOs-O)	542
OsO	462.3 ± 21	(Os-O)	575

Table 4

Molecular Constants of Os-O Species

Molecule	$I \times 10^{39}$ ($g\ cm^2$)	σ	g_0	ω_i (cm^{-1})
OsO_4	20.7 20.7 20.7	12	1	974, 340(2), 975(3), 335(3)
OsO_3	24.4 12.2 12.2	6	1	564, 347, 1040(2), 320(2)
OsO_2	16.2	2	3	900, 300(2), 800
OsO	7.0	1	10	885

Table 5

Gibbs Energy Functions of Os-O Species

	$-(G - H_{298})/T$, J K^{-1} mol^{-1}			
T/K	**OsO**	**OsO_2**	**OsO_3**	**OsO_4**
1000	272.2	287.4	321.1	337.3
1200	276.9	294.9	331.0	349.8
1400	281.1	301.8	340.0	361.3
1600	284.9	308.0	348.2	371.7
1800	288.4	313.7	355.6	381.3
2000	291.5	318.9	362.6	390.2
2200	294.5	323.8	369.0	398.4