MASS SPECTROMETRIC STUDIES OF GASEOUS OXIDES OF
RHENIUM AND OF THE LANTHANUM TRIFLUORIDE DIMER

Harry Bryant Skinner
(Ph. D. Thesis)

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MASS SPECTROMETRIC STUDIES OF GASEOUS OXIDES OF RHENIUM AND
OF THE LANTHANUM TRIFLUORIDE DIMER

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ABSTRACT

Knudsen cell mass spectrometry was employed in three temperature ranges (327-463°K, 1047-1267°K, and 1770-2143°K) to study the major vapor species present in the rhenium oxygen system. The sublimation of rhenium heptoxide was shown to yield rhenium heptoxide gas according to the pressure-temperature relationship

$$\log P_{\text{Re}_2\text{O}_7} = (7.437 \pm 0.081) \frac{10^3}{T} + (12.350 \pm 0.209)$$

where the pressure is in atmospheres. In addition, a small percentage of oxygen is evolved by incongruent vaporization according to the reaction

Weight loss measurements yielded $+13.204 \pm 0.250$ kcal for the enthalpy of the reaction at 298°K. Mass spectrometry of the vapors from the rhenium-zinc oxide reaction revealed evidence of $\text{ReO}_3(\text{g})$ and $\text{Re}_2\text{O}_6(\text{g})$. Measurement of the reaction of rhenium with zinc oxide as a function of temperature yielded values for the enthalpies of formation of $\text{ReO}_3(\text{g})$ and $\text{Re}_2\text{O}_6(\text{g})$ of -67.0 ± 3.5 kcal/mole and -209 ± 20 kcal/mole, respectively. Similar magnesium oxide-rhenium measurements confirmed the zinc oxide-rhenium measurements of the stability of $\text{ReO}_3(\text{g})$ and permitted upper limits to the dissociation energies of $\text{ReO}(\text{g})$ and $\text{ReO}_2(\text{g})$ to be established. Consideration of the data for each reaction argues against the presence of

of $\text{Re}_2\text{O}_5(\text{g})$, $\text{ReO}_2(\text{g})$ or $\text{ReO}(\text{g})$ as significant vapor species under any of the conditions of this study.

Intensities of ion peaks attributable to $\text{LaF}_3(\text{g})$ and $\text{La}_2\text{F}_6(\text{g})$ have been measured as functions of temperature in a mass spectrometer study of the equilibrium vapor of lanthanum trifluoride. The vaporization data for the monomer are in very good agreement with torsion-effusion data of Mar and Searcy. The heat of the reaction $\text{La}_2\text{F}_6(\text{g}) = 2\text{LaF}_3(\text{g})$ is 71.3 ± 0.9 kcal/mole at 1577°K . The apparent entropy of sublimation of the dimer is about 11 eu/mole lower than expected from studies of aluminum halides. It is argued that the principal ion fragment produced from $\text{La}_2\text{F}_6(\text{g})$ in the mass spectrometer is masked by that from $\text{LaF}_3(\text{g})$ and that the partial pressure of $\text{La}_2\text{F}_6(\text{g})$ is about 1% that of the monomer at 1575°K , a value about 100 times that calculated by conventional interpretation of the mass spectrometer data.

GENERAL INTRODUCTION

During the last ten years, literally hundreds of Knudsen cell mass spectrometric studies have appeared in the literature. As a result, thermodynamic data for many gaseous species have become available for temperatures even as high and higher than 2000°K. Unfortunately, despite the widespread application of mass spectrometry to thermochemical measurements some problems associated with electron impact ionization have not been resolved. The important problem for the present is fragmentation during electron impact, which can cause seriously misleading interpretations of the data. Fragmentation tends to mask the presence of the lower molecular weight species which are of particular importance at high temperatures. The principal objectives of this work were to seek evidence for the existence of rhenium oxide polymeric species similar to those found in chromium trioxide vaporization and to attempt to obtain data for possible lower oxygen content rhenium oxides.

Both objectives required dealing with the fragmentation questions. The extent of fragmentation is usually analyzed by two common methods.

- (1) examination of ionization efficiency curves and
- (2) measurements of apparent enthalpies of sublimation or reaction for parents and suspected fragments.

A subsidiary purpose of this study was to investigate the validity of these methods for molecules present in the vapor in small percentages.

That interpretation ionization efficiency curves might present problems has previously been noted. Mann[†] regarded use of monoenergetic electrons as a requirement for unambiguous interpretation of ionization efficiency curves, although few ion sources in use yield monoenergetic

electrons. In fact, Brion et al.[†] have noted that the energy spread of electrons from a hot filament, such as used in a mass spectrometer ion source is 1-2 eV, which obscures fine structure in the ionization efficiency curve.

Use of apparent enthalpies to resolve parent-fragment relationships is obviously limited by experimental error sufficient to easily disguise a parent which yields an ion with a concentration of the order of 10% of a fragment of the same mass.

Runs were made first on lanthanum trifluoride to learn mass spectrometric techniques and to check temperature measurements in the mass spectrometer. Lanthanum trifluoride was particularly well suited for this use because it was well characterized by vapor pressure measurements and appearance potential measurements. During this work, the lanthanum fluoride dimer was discovered and its stability was investigated. This work constitutes Part I of this thesis:

[†] See Reference 1, Part II

[‡] See Reference 2, Part II

PART I

DEMONSTRATION OF THE EXISTENCE OF La_2F_6 GAS AND
DETERMINATION OF ITS STABILITY

I. INTRODUCTION

Dimers are present at high concentrations in the vapors of aluminum trihalides but, although scandium, yttrium, and lanthanum trifluorides¹ and many lanthanide trifluorides²⁻⁴ have been studied with mass spectrometers, no dimers of these fluorides have been reported. By using effusion cells with multiple orifices of small diameter we have extended mass spectrometer measurements of lanthanum fluoride to higher temperatures and have measured as a function of temperature a low intensity peak that arises from dissociative ionization of La_2F_6 . This paper reports the measurements and compares the data obtained for $\text{La}_2\text{F}_6(g)$ with data for aluminum trihalide dimers⁵⁻⁷ and for double chlorides of alkali metals and lanthanide metals.⁸ Analysis of the enthalpy and apparent entropy data for the dimer leads to the conclusion that the true pressure of the dimer is not four orders of magnitude lower than that of the monomer as suggested by conventional interpretation of intensity data, but only about two orders of magnitude lower.

II. EXPERIMENTAL

This study was carried out with a 60° sector, 1 foot radius, magnetic deflection mass spectrometer built by Nuclide Associates. The sample of lanthanum trifluoride obtained from Semi-Elements, Inc. was heated by electron bombardment in a molybdenum Knudsen cell with a graphite liner. The lanthanum fluoride of this study was a nominal 99.9% purity, and showed .015% iron as the principle impurity by spectrographic analysis. The same material was used for the torsion-effusion portion of the study of Mar and Searcy.⁹

Three small orifices were employed in each lid to increase the ion current signal without exceeding the mean free path to diameter ratio above which molecular flow equations become invalid. The limiting ratio for LaF_3 gas has been demonstrated to be about 0.4 as calculated from the hard sphere model.⁹ Two orifice sizes were used, .01 cm diam. and .04 cm. diam. drilled in graphite cell lids of thicknesses .025 cm and .1 cm respectively. It should be noted that while some measurements were made close to the upper pressure limit for molecular flow, other measurements were made well below the limit. The molecules of the beam could not, therefore, have undergone the kind of adiabatic cooling with the resultant cluster formation that has recently been described.^{10,11} No shutterable species were observed at the mass numbers of LaF_3^+ or La_2F_6^+ , but peaks at masses corresponding to LaF_2^+ and La_2F_6^+ were concluded to be produced solely by dissociative ionization of the monomer $\text{LaF}_3(\text{g})$ and the dimer $\text{La}_2\text{F}_6(\text{g})$ respectively.

Identification of the species La_2F_5^+ was made by use of the calibrated gauss indicator to establish the mass as correct for La_2F_5^+ . A cell

exhaustion experiment proved that the La_2F_5^+ intensity dropped in conjunction with the LaF_2^+ intensity. Agreement of data from a graphite-lined tantalum cell with that from the graphite-lined molybdenum cell proved that a foreign metal did not contribute to the mass peak. Thermodynamic calculations indicate that contributions to LaF_2^+ and La_2F_5^+ ion intensities by reactions other than the main vaporization reactions should be negligible.

The intensities of the LaF_2^+ and the La_2F_5^+ ions were followed as a function of temperature using 70 eV ionizing electrons. Many data points were taken during each run with temperatures varied up, then down. Temperatures were measured with a Pt/Pt-90% Rh 10% thermocouple clamped securely to the molybdenum cell. About 15 min. was allowed between measurements to ensure that equilibrium had been reached.

It was necessary at high temperatures to follow the LaF_2^+ that resulted from contributions from the low abundance isotope La^{138} because intensities from LaF_2^+ that contained La^{139} were so high that they flooded the detector. All data were divided by the appropriate isotopic fractional abundance.¹²

The $\text{LaF}_3(\text{g})$ calculated from a least squares fit of the I^+T data of each run was made to coincide at the average temperature of the run with the lanthanum fluoride pressure of Mar and Searcy.⁹ The same factor, corrected for estimated relative cross sections and electron multiplier gain, was applied to the dimer intensity. The electron multiplier gain for the dimer was estimated to equal that of the monomer and the cross section for electron impact ionization for La_2F_6 was estimated to be 1.5 times the cross section of LaF_3 . This value is the approximate average found for dimers of alkali halides by Berkowitz et al.¹³

III. RESULTS AND DISCUSSION

Figure 1 shows the results of two mass spectrometer runs. Preliminary exploratory runs with the 0.01 cm diam. orifices gave data in reasonable agreement with the data of Fig. 1 but which were not included because instrumental variables were not as well controlled in the exploratory runs as in the subsequent runs.

Because the monomer data extend over a 500° range from 1221°K to 1736°K, the change in heat capacity for vaporization, ΔC_p , should not be neglected in calculation of enthalpies and entropies of vaporization. Mar and Searcy⁹ have estimated the heat capacity for the solid and monomer to be $C_p(s) = 19.796 + 8.42 \times 10^{-3} T - 5.90 \times 10^{-4} T^2$ and $C_p(\text{monomer}) = 21.323 - 4.065 \times 10^{-4} T - 3.375 \times 10^{-5} T^2$ respectively. The heat capacity difference for reactions, 2 monomer $\rightarrow$ dimer from JANAF⁵ for aluminum halides and iron chloride are all about 4 cal/deg.-mole of dimer. This constant 4 cal/deg.-mole of dimer was applied to give for sublimation of a mole of La_2F_6 $\Delta C_p = -11$ cal/deg. Second law enthalpies of sublimation were calculated for the monomer at 1487°K, the midpoint of the experimental range of Mar and Searcy⁹ and 1577°K, the midpoint of the range of measurements, to be 97.8 ± 0.8 kcal/mole and 96.7 ± 0.8 kcal/mole respectively. The enthalpy of sublimation at 1487°K for the monomer is in good agreement with the value of 99.3 kcal/mole of Mar and Searcy but only fair agreement with the value 92.0 kcal/mole reported by Kent et al.¹ at 1324°K. The calculated entropy of sublimation of the monomer at 1577°K is $42.03 \pm .72$ eu/mole.

From the least squares fit of the heat capacity-corrected data for the La_2F_6 molecule, the entropy and enthalpy of sublimation at 1577°K were calculated to be 38.4 ± 1.0 eu/mole and 122.1 ± 1.1 kcal/mole, respectively. The enthalpy and entropy of sublimation of monomers and dimers measured in this study yield a dimerization enthalpy for $\text{LaF}_3(\text{g})$ of -71.3 ± 1.9 kcal/mole and a dimerization entropy of -45.6 ± 1.8 eu/mole, where quoted error limits are standard deviations from the least squares fit.

Since temperature-dependent errors are easier to control in a torsion-effusion apparatus than in a mass spectrometer and since Mar and Searcy⁹ demonstrated careful temperature measurement by recording data on tin in good agreement with accepted values, their value of 99.3 kcal/mole at 1487°K should be accepted as the most reliable. Correction of our measured temperature dependences for the difference between this value and the value 97.8 that we measured at 1487°K yields a corrected value of 123.7 ± 5.0 kcal/mole for sublimation of the dimer at 1577°K . The same correction applied to the entropy of sublimation yields a value of 40.3 ± 3.0 eu/mole at 1577°K . The quoted error limits take into consideration uncertainties in measurement of relatively low pressures. These estimated limits yield probable error limits on the enthalpy and entropy of dimerization of ± 5.5 kcal/mole and ± 3.2 eu/mole, respectively.

Appearance potentials of ions observed in this work were determined by the method of extrapolated differences using Hg and are shown in Table 1. Our appearance potential data are in good agreement with that reported by Kent et al.¹ for fragments of the monomer.

The surprising result of this study is not that a dimer of a rare earth fluoride has been identified, but that its apparent concentration is so low -- the intensity of La_2F_5^+ is only about 10^{-4} times that of LaF_2^+ . In contrast Al_2F_6 is reported to constitute about 1.7% of the vapor of the aluminum trifluoride when the total vapor pressure is 10^{-5} atm. The aluminum chloride, bromide and iodide dimers vaporize at still higher relative concentrations. The enthalpy of dissociation of $\text{La}_2\text{F}_6(\text{g})$ to two $\text{LaF}_3(\text{g})$ molecules when the monomer pressure is 10^{-5} atm is 72.6 kcal compared to 48.8 kcal for $\text{Al}_2\text{F}_6(\text{g})$.⁷ The ratio of the enthalpy of sublimation of the monomer to the enthalpy of dissociation of the dimer to two monomers, which is usually critical in determining whether a dimer will be a major species,¹⁴⁻¹⁶ is 1.37 for the LaF_3 molecules compared to 1.38 for the AlF_3 molecules. The partial pressure calculated for La_2F_6 are anomalously low because of the exceptionally high entropy measured for dissociation of the La_2F_6 dimer to monomer. The exceptional entropy for La_2F_6 dissociation is apparent from Table II, which reports entropies for dissociation of the trihalide dimers and of alkali halide-metal trihalide molecules to the binary halides (for example, for $\text{KLaCl}_4(\text{g})$ dissociation to $\text{KCl}(\text{g})$ and $\text{LaCl}_3(\text{g})$).

In the absence of molecular structure and internal energy data which would permit calculation of entropies of the lanthanum fluoride vapor species by the methods of statistical mechanics, one cannot say with absolute certainty that the apparent entropy determined in this study is erroneous. But the anomalous entropy argues strongly that some systematic error was made either in measurement of $\text{La}_2\text{F}_5^+/\text{LaF}_2^+$ ion intensity ratios or in calculation of $\text{La}_2\text{F}_6/\text{LaF}_3$ pressure ratios from the measured intensities.

The most obvious possible source of such an error, failure to attain equilibrium for dimer vaporization, is ruled out by excellent agreement in intensity ratios measured with orifice areas that differed by a factor of 16.

The discrepancy could be explained by a breakdown in the proportionality rule:

$$P \propto I^+T$$

This possibility was suggested by Berkowitz et al.³ for lithium fluoride. The probable cause favored by those authors to explain the temperature trend in fragmentation of $\text{LiF}_{(g)}$ was the formation of Li^+ with excess kinetic energy. The very good agreement obtained in the present study for the temperature dependence of $\text{LaF}_{3(g)}$ pressures with that obtained by the torsion-effusion method implies that no such error exists for the monomer and, therefore, that such an effect would have to be an exclusive peculiarity of the dimer. To reconcile the measured intensity ratio with an expected entropy of ~ 35 for dimer dissociation to monomers would require that the efficiency of ionization at the highest temperature of measurement relative to that at the lowest temperature of measurement vary by a factor of about 5. Since significant temperature dependences for fragmentation have not been clearly established for any high temperature systems, such a large variation in ionization efficiency seems highly improbable. Furthermore, a less drastic explanation of the anomalous data is provided by comparison with fragmentation patterns for complex salt molecules.

Table III lists fragmentation patterns reported for several complex molecules for which the principal ion has been identified as a small fragment of the parent molecule. In each of these examples, the reaction that seems most reasonable to explain production of the observed ion from the singly ionized parent molecule is one that yields the observed ion, a

halogen atom, and a neutral monomer of one of the constituent salts.

For example,

It is well established¹⁷ that a sequence of monomolecular dissociation reactions can give rise to several fragments of the parent ion such as indicated in reaction 1. The analogous reaction for the lanthanum fluoride dimer would be

It is reaction 2, rather than $\text{La}_2\text{F}_6^+ = \text{La}_2\text{F}_5^+ + \text{F}$, which from behavior of related polymeric species under electron bombardment would be expected as the principal reaction of an excited La_2F_6^+ ion. But this reaction is masked by the higher LaF_2^+ intensity from LaF_3^+ fragmentation.

The appearance potential for LaF_2^+ from reaction 2 can be calculated from the enthalpy of dissociation of the dimer to monomer and from the appearance potentials of La_2F_5^+ and LaF_2^+ to be 14.9 eV compared to 11.8 eV for LaF_2^+ from the monomer. The occurrence of reaction 2, therefore, would not be revealed by measurement of LaF_2^+ intensities as a function of electron energies.

We conclude that reaction 2 is probably the principal reaction undergone by La_2F_6 when ionized by 70 eV electrons. The temperature dependence for vaporization of the dimer calculated from La_2F_5^+ intensity measurements and the enthalpy of dissociation of dimer to monomer and of sublimation of the dimer derived from that temperature dependence are correct. The partial vapor pressure of the dimer is best estimated by assuming the entropy

of dissociation of dimer to monomer to be about the same as for Al_2F_6 , 35 eu per mole of dimer, from which the partial pressure of La_2F_6 dimer is calculated to be 6.2×10^{-8} atm. when the partial pressure of the monomer is 10^{-5} atm. Figure 1 shows the estimated true pressure of the dimer.

We plan next to study $\text{Ce}_2\text{F}_6(\text{g})$. We anticipate that the extra electron of each cerium atom will give rise to a small increase in stability of the dimer relative to the monomer and will cause a change in fragmentation patterns¹⁸ for both monomer and dimer. A higher intensity of dimer would, and a changed fragmentation pattern could, make easier the problem of analysis of the monomer-dimer stability relationships. The cerium fluoride study should, therefore, not only be interesting in itself but should strengthen or weaken the credibility of the analysis we have presented of our lanthanum fluoride data.

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TABLE I

Appearance potentials of ions in the mass spectra of $\text{LaF}_3(\text{g})$.

Ion	This work (eV)	Kent et al. (eV)
La^+	26.9	26.5
LaF^+	18.5	18.5
LaF_2^+	11.8	12.0
La_2F_5^+	12.4	

TABLE II Entropy changes for the reactions $2 \text{MX}_3(\text{g}) \rightarrow (\text{MX}_3)_2(\text{g})$ and $\text{NX}(\text{g}) + \text{MX}_3(\text{g}) \rightarrow \text{NMX}_4(\text{g})$ in the experimental temperature range.

Associated Compounds	$-\Delta S$ (eu)	Reference
$(\text{AlI}_3)_2$	33.9	5
$(\text{AlCl}_3)_2$	34.3	5
$(\text{AlBr}_3)_2$	37.4	5
$(\text{AlF}_3)_2$	35.0	6,7
$(\text{LaF}_3)_2$	45.6	this work
$(\text{FeCl}_3)_2$	33.9	5
NaLaCl_4	32.8 ± 1.8	8a
NaNdCl_4	33.3	8b
NaErCl_4	34 ± 5	8c
KLaCl_4	32 ± 9	8d
KCeCl_4	32.6 ± 3	8d
KPrCl_4	32.6 ± 3	8d
KNdCl_4	32.6 ± 3	8d
KErCl_4	32.6 ± 2	8e
CsNdCl_4	29.8	8b
CsErCl_4	30.8	8b

TABLE III Fragmentation patterns for some complex molecules

Parents	Observed Ions	Intensity	Reference
KCl-ErCl ₃ (30V electrons)	K ⁺	59	8f
	KCl ⁺	0.76	
	Er ⁺	0.63	
	ErCl ⁺	0.56	
	ErCl ₂ ⁺	1.9	
	KErCl ₂ ⁺	0.16	
	KErCl ₃ ⁺	1.0	
CsCl-ErCl ₃ (52V electrons)	Cs ⁺	67.6	8b
	CsCl ⁺	.88	
	Cs ₂ Cl ⁺	.96	
	ErCl ₂ ⁺	.79	
	CsErCl ₂ ⁺	.04	
	CsErCl ₃ ⁺	1.0	
CsCl-NdCl ₃ (51V electrons)	Cs ⁺	526	8b
	CsCl ⁺	5.84	
	Cs ₂ ⁺	.26	
	Cs ₂ Cl ⁺	4.58	
	Nd ⁺	1.05	
	NdCl ⁺	1.74	
	NdCl ₂ ⁺	6.05	
	NdCl ₃ ⁺	0.16	
	CsNdCl ₂ ⁺	0.05	
	CsNdCl ₃ ⁺	1	
LiBeF ₃ (60V electrons)	Li ⁺	2.9	19
	LiBeF ₂ ⁺	1	
	LiF ⁺	.06	
Li ₂ BeF ₄ (60V electrons)	Li ₂ F ⁺	40	19
	Li ₂ BeF ₃ ⁺	1

XBL703-2600

Figure 1.. Vaporization data for lanthanum trifluoride.

PART II

MASS SPECTROMETRIC STUDIES
OF CASEOUS OXIDES OF RHENIUM

I. INTRODUCTION

The vaporization of condensed ReO_3 and ReO_2 was first investigated mass spectrometrically by Semenov and Ovchinnikov.³ In a later investigation, Battles, Gunderson and Edwards⁴ showed that $\text{ReO}_3(\text{s})$ and $\text{ReO}_2(\text{s})$ do not vaporize congruently as reported by Semenov and Ovchinnikov.³ In addition, Battles et al.⁴ found that $\text{Re}_2\text{O}_7(\text{g})$ was the major vapor species over mixtures of ReO_3 - ReO_2 and of ReO_2 -Re. Work by Norman, Winchell and Staley⁵ resulted in two widely divergent values for the stability of $\text{ReO}_3(\text{g})$. Either value, however, indicated that $\text{ReO}_3(\text{g})$ might be present in small concentrations, so a search for the existence of ReO_3 provided an ideal subject to study.

This study of the rhenium oxygen system consists of three parts. The first is a study of the vaporization of rhenium heptoxide. The second and third are studies of the reaction of rhenium with zinc oxide and magnesium oxide, respectively.

II. RHENIUM HEPTOXIDE VAPORIZATION

A. Experimental

This study was carried out with a 60° sector, 1 foot radius, magnetic deflection mass spectrometer built by Nuclide Analysis Associates. The rhenium heptoxide obtained from Alfa Inorganics Co. showed Mg to be the only detectable impurity by semi-quantitative spectroscopic analysis:

The sample was resistively heated by nichrome wire wound closely around an anodized aluminum Knudsen cell. If the Re_2O_7 came in contact with the aluminum cell, maroon or black contaminants, probably ReO_2 or ReO_3 , were found in the cell after heatings. To eliminate the problem, the interior of the cell was gold plated and a gold lid and liner were installed which prevented any contact of the Re_2O_7 with the aluminum.

Several experiments following this change were performed in which the solid Re_2O_7 appeared unchanged after vaporization. Color changes still occasionally occurred however, indicating reactions other than the primary sublimation reaction. Weight loss experiments were then carried out to determine whether Re_2O_7 vaporized congruently. These experiments were performed in a separate vacuum system capable of $\sim 2 \times 10^{-6}$ torr. The Knudsen cell and liner from the mass spectrometric experiments were used.

Weight loss measurements were made on rather large samples (~ 0.5)g to obtain measurable residues and to minimize end effects. The samples were vaporized to dryness by heating the cell to temperature and holding until some 8-12 hours after the cell was calculated to be exhausted. The cell was then weighed, replaced, and heated for 12-24 hours. As many as two repetitions were required to achieve constant weight.

The currents of all ions produced by bombardment of the vapor from Re_2O_7 solid by 70 eV electrons, Re_2O_7^+ , Re_2O_6^+ , Re_2O_5^+ , ReO_3^+ , ReO_2^+ were measured seven or more times over a seven day period while the rhenium heptoxide was held at about 404°K . Measurements used in determining an average intensity for each ion relative to Re_2O_7^+ were only made after the intensities had reached steady state values (about two days). Appearance potentials were measured for each of these ions by the method of extrapolated differences. The mercury background ion intensity was used as the reference. Analysis of these data and comparison with data for the same ions produced by reaction of rhenium metal with metal oxides showed all the lighter ions from Re_2O_7 solid to result primarily from fragmentation of a $\text{Re}_2\text{O}_7(\text{g})$ parent molecule when vaporization of solid rhenium heptoxide was studied (see discussion section).

The intensity of the Re_2O_7^+ ion produced by 70 eV electrons was followed as a function of temperature from 327°K to 463°K . Three runs were made, with several datum points being taken in each run in a random manner allowing 1/2 hour or more for equilibrium to be obtained. A 0.0762 cm diameter effusion orifice was used for two of the runs and a 0.014 cm orifice for the higher temperature run. Channel lengths were about equal to the orifice diameters. The temperature was continuously monitored and readings were taken after at least 15 min. had passed with the temperature constant to within $1/2^\circ$. Two 5 mil. chromel-alumel thermocouples were used. One was placed between the gold cell lid and the gold cell lip. The other was clamped to the cell ~1.6 mm from the bottom. The two thermocouples read to within $1/4^\circ$ of each other. The thermocouples were calibrated by determination of the melting point of Indium (99.999%). They gave melting

points of 429.98°K and 430.27°K. The value listed by Stull and Sinke⁶ is 429.32°K.

Since the heat of sublimation was to be determined from the temperature dependence of the measured ion intensities, the heat of sublimation of cadmium was measured by the same (second law) method to test the reliability of the apparatus and experimental techniques. Nine datum points were taken in random order over the temperature range 427 to 512°K. A least square enthalpy of $26.72 \pm .52$ kcal/mole (where the quoted error is the standard deviation), was calculated from the data. This value is in good agreement with Hultgren's⁷ selected value at 469°K, $26.41 \pm .15$ kcal/mole.

B. Results

The measurements of the relative intensities of the major species observed over Re_2O_7^+ are shown in Table I. Re_2O_6^+ and Re_2O_5^+ changed little relative to Re_2O_7^+ in the initial days of vaporization. The relative intensities of ReO_2^+ and particularly ReO_3^+ decreased appreciably. The steady state ion current found for ReO_3^+ was found for ReO_3^+ was about 30% smaller than the initial value. This change is attributed to gradual reduction in contamination by HReO_4 from which ReO_3^+ and ReO_2^+ would arise through a fragmentation process. Appearance potentials are compared in Table II to those measured by Battles et al.⁴

Data for the steady state Re_2O_7^+ ion are plotted in Fig. II-1. Also shown are the previous total pressure measurements of Glemser et al.⁸ and Smith et al.⁹

In the highest temperature run the two highest temperature points appeared to yield erroneously high pressures, probably because of breakdown

of molecular flow conditions.¹⁰ The ratio of mean free path to orifice diameter were calculated by the use of the hard sphere approximation to be for these two points 0.53 and 0.73. They were discarded from the enthalpy calculations.

The vapor pressure of Re_2O_7 from 327°K to 463°K is given by the equation

$$\text{Log } P_{\text{atm}} = (7.437 \pm .081) 10^3/T + (12.350 \pm .209)$$

where the quoted error are the standard deviations from the least squares fit.

Weight loss experiments show that while $\text{Re}_2\text{O}_7(\text{s})$ vaporizes predominantly to $\text{Re}_2\text{O}_7(\text{g})$, some O_2 gas is also evolved so a residue is left which was identified as $\text{ReO}_3(\text{s})$ by x-ray diffraction (see Table III). Semi-quantitative spectroscopic analysis of the residue showed principle impurities to be Mg, Si and Fe, present to less than 2%. Quantitative data were obtained by using the total weight loss due to $\text{Re}_2\text{O}_7(\text{s})$ vaporization to calculate the time of vaporization. This value and the weight of $\text{ReO}_3(\text{s})$ remaining permitted calculation of the pressure of the oxygen which had effused out of the cell. The weight loss data used to calculate the oxygen pressures for the reaction

are given in Table IV. The calculated oxygen pressures are shown on Fig. 1.

It was necessary to estimate the free energy functions for both $\text{Re}_2\text{O}_7(\text{s})$ and $\text{ReO}_3(\text{s})$. The heat capacity for $\text{Re}_2\text{O}_7(\text{s})$ was estimated to be linear from the value given by Busey¹² at 298°K to the melting point where the C_p was estimated to be 7.0 cal/deg atom. This gave $C_p = 14.55 + 8.47 \times 10^{-2} T$.

The value of $S_{298}^{\circ} = 19.3$ eu/mole has been reported for $\text{ReO}_3(\text{s})$ by King and Cobble.¹¹ The heat contents and entropy increases above 298°K for $\text{ReO}_3(\text{s})$ were assumed to be the same as the values reported for $\text{WO}_3(\text{s})$ were assumed to be the same as the values reported for $\text{WO}_3(\text{s})$ in JANAF.¹⁵ JANAF¹⁵ data were used for $\text{O}_2(\text{g})$.

The enthalpy and entropy of sublimation of $\text{Re}_2\text{O}_7(\text{s})$ were calculated in the following manner. The least squares fit of each run was made to coincide at the average pressure of Glemser et al.⁸ and Smith et al.⁹ at 433.3°K. Enthalpies calculated from temperature dependence of intensities for the three runs were 33.252 ± 0.716 kcal/mole, 35.301 ± 0.152 kcal/mole, and 36.448 ± 0.916 kcal/mole. The least squares fit of all the data normalized to this point yielded an enthalpy of sublimation of 34.024 ± 0.370 kcal/mole and an entropy of sublimation of 56.60 ± 0.96 eu/mole.

The calculated Gibbs free energies at temperature and values of ΔH_{298}° for Reaction (1) are summarized in Table V. The ΔH_{298}° of each calculated O_2 dissociation pressure was estimated to have approximate error limits of 1/2 kcal, yielding a heat of 13.204 ± 0.250 where the quoted error is the probable error of the mean.

III. ZINC OXIDE RHENIUM EQUILIBRIUM

A. Experimental

The reagent grade zinc oxide supplied by Baker and Adamson which was used in this part of the study showed the following impurities by semi-quantitative spectroscopic analysis:

Si	.06%
Mn	.15%
Fe	.008%
Mg	.007%
Al	.005%
Cu	.002%
Ca	.025%

For most of the experiments, zinc oxide was sintered before use for several days at $\sim 500^{\circ}\text{C}$ to remove adsorbed water. The rhenium powder obtained from the Department of Chemistry, University of Tennessee showed

Si	.015%
Al	.005%
Mg	.000%
Cu	.002%
Ca	.003%
Ag	.008%

as impurities by spectroscopic analysis. Analyses were performed by American Spectrographic Laboratories, San Francisco. X-ray diffraction examination of the sample showed only zinc oxide and Re, as was expected. Mass spectrometer experiments were performed in a molybdenum or tantalum outer cell with either an alumina cell liner or a rhenium liner. Because neither cell was gas tight, a machined alumina cell was constructed for weight loss experiments. Orifice areas were smaller by a factor of ~ 10 than those u

by Anthrop¹⁶ to obtain equilibrium data in zinc oxide vaporization. Heating at lower temperatures was by radiation from two filaments positioned horizontally around the cell at top and bottom to minimize gradients along the length of the cell and at higher temperatures was by electron bombardment. The temperature was measured to the nearest degree with a platinum/ platinum 10% rhodium thermocouple clamped to the bottom of the cell.

Temperature calibrations were checked by measuring the second law enthalpy of sublimation of silicon in the range 1051 to 1225°K. Fourteen datum points which were taken in random order yielded a least squares enthalpy of sublimation $64.48 \pm .44$ kcal/mole at 1138°K in fair agreement with the value of 66.49 ± 20 kcal/mole at 1138°K, interpolated from Hultgren's tabulation.⁷

Otvos and Stevenson¹⁷ cross sections for electron impact ionization were used in this work with the assumption that atomic cross sections are additive. Cross sections and relative electron multiplier gains are given in Table VI.

The intensity of each ion produced with 70 eV electrons was followed as a function of temperature. Many datum points were taken in each of five runs. After the temperature had stabilized, about 15 min. was allowed for equilibrium to be obtained.

In all temperature variation experiments, a small portion of zinc metal was added to the rhenium zinc oxide. Measurement of the $\text{Zn(s)} \rightarrow \text{Zn(g)}$ equilibrium at low temperature provided a direct calibration for determining the proportionality constant between I^+ and pressure. Several Zn^+ intensities were measured, then the zinc was exhausted and the rhenium zinc oxide equilibrium was measured.

In addition, weight loss experiments were performed. For these experiments the temperature was raised as quickly as possible to the desired temperature and stabilized. The ion intensities corresponding to molecules that cause the weight loss were measured several times during a run and averaged in order to calculate equilibrium constants. Runs were terminated by shutting off the power. Both heating and cooling end effects were estimated to be negligible.

To check the accuracy of the weight loss experiments, two weight loss measurements were made on silver. The results of these experiments are shown in Table VII. Experimentally measured silver pressures were found to be approximately 1.74 times higher than the pressures selected by Hultgren.⁷ The measured total pressure in the rhenium-zinc oxide weight loss experiments was reduced by this factor to correct for systematic errors.

Appearance potential measurements were made on Re_2O_6^+ , Re_2O_5^+ , ReO_3^+ and ReO_2^+ ions found arising from the vapor above zinc-oxide rhenium mixtures. One set of measurements was made using background mercury as a standard, another used Zn^+ from the reduction of zinc oxide to zinc vapor. Because ReO_3 was suspected of arising from both dissociative ionization and simple ionization, its ionization efficiency curve was measured at two temperatures. It was hoped that a distinct break similar to that reported by Grimley¹⁸ for CrO in the chromium oxygen system would be obvious from direct comparison of the curves at temperatures in which the portion due to fragmentation was calculated to be minor (~29%) and calculated to be predominant (~57%).

A cell exhaustion experiment was done to determine if the $\text{Re}_2\text{O}_6(\text{g})$ is present in significant amounts in the gas phase above zinc oxide-rhenium. For this

experiment, excess rhenium powder was mixed with a very small portion of zinc oxide powder. The mixture was heated to about 1186°K and held until the intensities began to drop. The intensities of Re_2O_7^+ and Re_2O_6^+ were followed as a function of time. When the intensities had dropped to about 1/10 of their initial values, the cell temperature was raised about 50° causing the intensities to increase. The intensity of each ion was again followed at constant temperature until the Re_2O_6^+ intensity had dropped to a value which was difficult to measure in a time span of 1 minute. This process was repeated until at about 1450°K the Re_2O_6^+ ion intensity became too small for accurate measurements.

B. Results

Results of appearance potential measurements are shown in Table VIII. A plot of ReO_3^+ ionization efficiency curves up to 25 eV taken at 1191°K and 1313°K is shown in Fig. 2. The curves were brought into approximate coincidence by adjusting the electron multiplier gain to yield approximately the same ion intensities at 70 eV.

The average of several separate measurements of the major ion intensities above rhenium-zinc oxide mixtures are given in Table IX. Comparison of these intensities to Table I show a significant increase in all the intensities. Plots of the intensities of the Re_2O_6^+ and Re_2O_7^+ with no corrections for fragmentation were prepared showing the initial decline of intensities and each succeeding decline on temperature rise. No significant pressure dependence of intensities with time was found. However little pressure dependence would be expected in a pressure variation of a factor of 10, since the ratio of pressures depends only on the square root of the oxygen pressure and the independence of the Re_2O_6^+ is

masked by a fragmentation contribution from $\text{Re}_2\text{O}_7(\text{g})$ amounting to greater than half of the total Re_2O_6^+ intensity. However each temperature increase reduced the oxygen activity further and constant temperature ratios measured over a period of time showed a steady decrease. The observed ratio of Re_2O_7^+ to Re_2O_6^+ during the initial decline at 1186°K was ~ 9.4 . On increasing the temperature to 1235°K , 1298°K , 1353°K and 1407°K this ratio dropped to ~ 8.5 and ~ 7.9 and ~ 7.5 and 7.2 . Heating to 1436°K , The $\text{Re}_2\text{O}_7^+/\text{Re}_2\text{O}_6^+$ ratio was found to be ~ 6.5 and the $\text{ReO}_3^+/\text{Re}_2\text{O}_7^+$ ratio was found to be 10.

The slopes of the $\log I^+T$ vs $1/T$ plots of a typical run at 70 eV for intensities with no fragmentation correction were for Re_2O_7^+ : 58.25 ± 0.68 , Re_2O_6^+ : 59.53 ± 0.92 , and ReO_3^+ : 64.30 ± 0.66 , all in kcal. ReO_2^+ and Re_2O_5^+ ions did not have slopes significantly different from those of ions of heavier masses from which the two lighter ions were probably produced by fragmentation.

Analysis of the preceding data (see discussion) demonstrated that the only important neutral precursors of all rhenium containing ions were $\text{Re}_2\text{O}_7(\text{g})$, $\text{ReO}_3(\text{g})$ and $\text{Re}_2\text{O}_6(\text{g})$. To calculate pressures of these species the ion currents for each run were corrected for differences in electron multiplier gain. The proportion of each ion current due to fragmentation of Re_2O_7 (Table I) was subtracted from the total ion current for that ion. The currents were then multiplied by temperature and divided by cross-section. From these, equilibrium constants were calculated.

The results of the weight loss experiments on Rhenium-zinc oxide mixture are shown in Table X and the equilibrium constants are plotted on figures 3, 4, and 5. Results of temperature variation experiments are also shown in

Figs. 3, 4, and 5. Initial plotting of data using calibration factors from measurement of zinc vapor pressure showed considerable scatter in the entropies of reaction. Weight loss measurements (Table X) showed fair agreement with the three experiments which yielded the highest calculated pressure. (See Fig. 3). The discrepancy in the other two experiments can be explained if the zinc pressures measured for calibration were about a factor of 5 low for those two runs. Such an error was possible because only small amounts of zinc were used and equilibrium zinc pressures may not have been developed in the cells.

All mass spectrometer runs were adjusted to coincide with the weight loss experiments by using the least squares enthalpy for each run to calculate an average entropy for that run. The enthalpies of equilibrium constant measurements on the reaction

were corrected by the error found in measuring the enthalpy of sublimation of silver. The correction for the above reaction is 16.0 ± 3.5 kcal/mole, yielding an average enthalpy of 516.5 kcal/mole at 1156°K. An internal check on the corrected enthalpy can be made since the heat of formation of $\text{Re}_2\text{O}_7(g)$ can be calculated from the heat of vaporization of $\text{Re}_2\text{O}_7(g)$ and the heat of formation of $\text{Re}_2\text{O}_7(s)$. When temperature corrections are made using data from K. K. Kelley¹⁹ for $\text{Re}(s)$, $\text{ZnO}(s)$, and $\text{Zn}(g)$ and the approximation that the heat content for $\text{Re}_2\text{O}_7(g)$ is that given by JANAF for $\text{W}_2\text{O}_6(g)$ the heat for reaction (1) is calculated to be of 521.3 ± 3.0 kcal. This is in good agreement with the corrected value of 516.5 kcal.

Enthalpies and average entropies calculated from the equilibrium constant measurements for the three equilibria, are corrected for the error found in measuring the enthalpy of sublimation are shown in Table XI.

The average enthalpies calculated by weighting each enthalpy by the number of points in that particular run were used to calculate the entropies of reaction using the weight loss measurements.

The heats of formation of $\text{ReO}_3(\text{g})$ and $\text{Re}_2\text{O}_6(\text{g})$ at 298°K were calculated by the second and third law methods. (Table XII). For $\text{ReO}_3(\text{g})$ estimated free energy function and heat content values were available.²⁰ For Re_2O_6 , the thermochemical values given by JANAF¹⁵ for W_2O_6 were used. The heat of formation for zinc oxide employed in this calculation was 111.8 kcal/mole at 1156°K . Additional auxiliary data for $\text{Re}(\text{s})$ and $\text{O}_2(\text{g})$ were taken from Kelley.¹⁹

IV. THE MAGNESIUM OXIDE-RHENIUM EQUILIBRIUM

A. Experimental

The magnesium oxide used in this portion of the study was obtained from single crystals of unknown origin. Semi-quantitative spectroscopic analysis revealed only the following impurities: Si 0.008%, Fe 0.007%, Ca 0.01%, Mn 0.001%, Al 0.001%, and Cr 0.001%. The crystals were ground in a silica mortar and pestle immediately before use. X-ray diffraction of the sample after vaporization showed no evidence of phases other than magnesium oxide and rhenium.

A tungsten outer cell and top with a 0.08 cm orifice surrounded a rhenium cell liner. Three filaments were used rather than two, with the third one being placed slightly above center to ensure that the orifice was hotter than the bottom and to enable three blackbody holes (with length to diameter ratio of 4 to 1) to be seen with an optical pyrometer from outside the mass spectrometer. The optical pyrometer was calibrated through the window used in the experiments against a standard optical pyrometer by the Lawrence Radiation Laboratory meter shop. To enable temperature gradients expected from this procedure to be compensated for, the second law enthalpy of sublimation of lanthanum metal was measured in the temperature range 1794°K to 2103°K. Ten datum points yielded a least squares ΔH_{1950} of 93.4 ± 1.7 kcal/mole, only in fair agreement with the value of 99.7 ± 1.0 kcal/mole interpolated from Hultgren's⁷ tabulation.

The two temperature variation experiments were conducted in a similar manner to those on zinc oxide and rhenium at 70 eV electrons. Random variation of temperature with no trend in intensities indicated attainment of equilibrium. Appearance potentials were measured using background mercury as a standard for the extrapolated differences method.

B. Results

Ions at masses corresponding to Mg^+ , ReO_3^+ , ReO_2^+ , and ReO^+ were observed in the approximate intensity ratio of 5.5:1:0.32:0.10 respectively. No shutterable peaks which could be attributed to Re_2O_5^+ , Re_2O_6^+ , or Re_2O_7^+ were found at intensities of 0.1% of the ReO_3 peak at 2080°K. The appearance potentials of ReO_3^+ , ReO_2^+ and ReO^+ were found to be 12.5 ± 0.4 eV 14.4 ± 1.0 eV and about 18 eV. Apparent enthalpies of reaction for one of the runs were for ReO_3^+ : 108.9 ± 2.6 kcal/mole, ReO_2^+ : 113.9 ± 2.9 kcal/mole and ReO^+ : 115.4 ± 2.9 kcal/mole where the quoted errors are the standard deviations from the least squares fit of the data.

From these data, it is concluded that ReO^+ and ReO_2^+ arise primarily from dissociative ionization of $\text{ReO}_3(\text{g})$ (see discussion). Quantitative data may be derived only from the ReO_3^+ measurements which are shown plotted in Fig. 6 as the equilibrium constant for the reaction of magnesium oxide with rhenium metal to yield rhenium trioxide gas. Least squares fitting of the two runs yields heat of reaction of 425.9 ± 5.1 kcal/mole and 429.1 ± 5.7 kcal/mole. These enthalpies are corrected to 451.1 ± 7.2 kcal/mole and 454.3 ± 7.6 kcal/mole, when compensation is made for the difference between the accepted enthalpy of sublimation of lanthanum metal and the value obtained in this work. The average enthalpy of 452.7 ± 5.2 kcal yields a heat of formation at 1980°K of -69.6 ± 5.0 kcal/mole $\text{ReO}_3(\text{g})$ when combined with the JANAF¹⁵ value for the heat of formation of magnesium oxide.

V. DISCUSSION

Performing experiments over a wide range of temperatures on one system provides an excellent opportunity to prove, primarily on thermodynamic grounds, which ionic species actually arise at least to some extent from simple ionization. Proof of the presence or absence of each molecule in a particular temperature range of this work is most conveniently given by considering the highest temperature magnesium oxide-rhenium experiments first. Enthalpy measurements for the reaction

with the assumption that there is no contribution to ReO^+ , ReO_2^+ , or ReO_3^+ by fragmentation yield either the heat of formation or an upper limit on the heat of formation of ReO , ReO_2 , and ReO_3 .

The results at 1980°K are for

$$\text{ReO}_3(\text{g}) \Delta H_f = 69.6 \pm 5.0 \text{ kcal/mole}$$

$$\text{ReO}_2(\text{g}) \Delta H_f > -5.5 \pm 5.0 \text{ kcal/mole}$$

$$\text{ReO(g)} \Delta H_f > 51.8 \pm 5.0 \text{ kcal/mole.}$$

The enthalpy for ReO_3 is unambiguous because no detectable higher mass ions of the kinds found for Re_2O_7 sublimation were observed. The upper limit on the heat for $\text{ReO}_2(\text{g})$ from the magnesium oxide-rhenium measurements indicates a stability greater by 20 kcal than the heat of formation reported for $\text{WO}_2(\text{g})$ by JANAF¹⁵ and the limit placed on ReO(g) is more negative by 50 kcal than the JANAF¹⁵ value for WO(g) .

These values then allow upper limits to be placed on the pressure of $\text{ReO}_2(\text{g})$ and $\text{ReO}(\text{g})$ in the rhenium-zinc oxide experiments. Using entropies for the comparable tungsten molecules from JANAF¹⁵ and the pressure of zinc found from the weight loss experiment at 1187°K, one calculates very conservative maximum pressures for $\text{ReO}_2(\text{g})$ and $\text{ReO}(\text{g})$ of 3×10^9 atm. and 7×10^{-10} atm. respectively, compared to a pressure of 2×10^{-6} atm for $\text{Re}_2\text{O}_7(\text{g})$. The value of the heat of formation of $\text{ReO}_3(\text{g})$ from the magnesium oxide-rhenium experiments is found to be close to that measured in experiments with zinc oxide-rhenium mixtures.

Observations in the zinc oxide rhenium experiments suggests that ReO_3^+ arose in part from simple ionization and in part from fragmentation. The fact that the ratio $\text{ReO}_3^+/\text{Re}_2\text{O}_7^+$ is intermediate between that found for sublimation of $\text{Re}_2\text{O}_7(\text{s})$ and for the higher temperature magnesium oxide plus rhenium reactions supports this conclusion.

A comparison of appearance potential measurements at low temperatures and high temperatures (Tables II and VIII) clearly show that while $\text{Re}_2\text{O}_7(\text{g})$ is the probable parent of all ReO_3^+ observed during $\text{Re}_2\text{O}_7(\text{s})$ vaporization, either $\text{ReO}_3(\text{g})$, $\text{Re}_2\text{O}_6(\text{g})$, or $\text{Re}_2\text{O}_5(\text{g})$ is an additional parent of ReO_3^+ (and ReO_2^+) in the zinc-oxide - rhenium experiments. The appearance potential measured from the zinc oxide - rhenium experiments for ReO_3^+ is lower than that found when $\text{Re}_2\text{O}_7(\text{s})$ is the vapor source but still higher than that reported by Norman et al.⁵ (12.4 eV) or Rovner et al.²¹ (11 eV). For either Re_2O_5^+ or Re_2O_6^+ to be a significant parent of ReO_3^+ in the zinc oxide plus rhenium reaction would require temperature dependent fragmentation since intensities of neither Re_2O_5^+ nor Re_2O_6^+ increased as markedly as intensities of ReO_3^+ under reducing conditions. Because neither Re_2O_6^+

nor Re_2O_5^+ showed a $\log I^+T$ vs $1/T$ slope significantly different from that of Re_2O_7^+ in the zinc oxide - rhenium experiments while ReO_3^+ did, it seems clear that Re_2O_6^+ and Re_2O_5^+ were largely fragments from Re_2O_7 while the ReO_3^+ arises at least in part from simple ionization of ReO_3 .

However, either temperature-dependent fragmentation occurs of $\text{Re}_2\text{O}_6(\text{g})$ is present at about 1% of the pressure of $\text{Re}_2\text{O}_7(\text{g})$. We favor the conclusion that Re_2O_6 is present since the cell exhaustion experiment also shows $\text{Re}_2\text{O}_6^+(\text{g})$ intensities to vary independently from Re_2O_7^+ . While the cell exhaustion experiment could not and did not reveal striking changes in the $\text{Re}_2\text{O}_6^+/\text{Re}_2\text{O}_7^+$ ratio, since the two molecules have only slightly different oxygen partial pressure dependences, the cell exhaustion did offer an opportunity to measure the intensities of the two ions in a single, closely controlled experiment in which thermodynamic quantities were the only variables. The kind of increase in ratio expected from thermodynamics was observed.

$\text{Re}_2\text{O}_5(\text{g})$ may possibly be a parent of some of the Re_2O_5^+ measured in the rhenium-zinc oxide experiments but can be present only in low concentrations. Any Re_2O_5^+ not accounted for by fragmentation of $\text{Re}_2\text{O}_7(\text{g})$ could be a fragment from Re_2O_6 . The true pressure of Re_2O_5 is probably much less than 1% of the $\text{Re}_2\text{O}_7(\text{g})$ pressure.

The enthalpies of formation or their upper limits obtained from equilibrium studies can be used to calculate "maximum pressures" for each possible vapor species in the $\text{Re}_2\text{O}_7(\text{s})$ vaporization. These maximum pressures for all species other than $\text{Re}_2\text{O}_7(\text{g})$ are far lower than would be calculated from the measured intensity ratios in $\text{Re}_2\text{O}_7(\text{s})$ vaporization on

the assumption that the observed ions are produced by simple ionization of parents of the same mass as the observed ion. The good agreement between the enthalpy calculated from Re_2O_7^+ ion data and the enthalpies calculated from total pressure measurements of Glemser et al.⁸ and Smith et al.⁹ also indicates that other gaseous species are minor.

Vapor density measurements of $\text{Re}_2\text{O}_7(l)$ by Niselson et al.²² which became available while the present study was in progress, indicate a molecular weight of 482 g/mole at 685°K, a value which confirms our conclusion that the vapor over Re_2O_7 is monomeric $\text{Re}_2\text{O}_7(g)$.

The ion intensities of Table I clearly, then provide the fragmentation pattern for $\text{Re}_2\text{O}_7(g)$, and correction of intensity ratios measured in the zinc oxide-rhenium experiments (Table IX) for Re_2O_7^+ fragmentation provides intensities for ReO_3^+ and Re_2O_6^+ from which stabilities of the neutral molecules of the same mass numbers can be calculated.

The second and third law heats calculated for ReO_3 and Re_2O_6 from the corrected data are only in fair agreement. Two explanations can be put forward for this difference. The first invokes a possible error in the free energy function. Larger free energy functions for ReO_3 and Re_2O_6 would bring the second law the third law heats into better agreement. Neither free energy function used for these calculations included an electronic contribution. Brewer and Chandrasekharaiah²³ have approximated electron contributions for monoxides by assuming the oxide ion perturbs the metal ion very little. They then use the energy levels of the (+2) cation, which for ReO contributes 3.6 eu to the free energy function. If an electronic contribution this large were applied to the free energy function of ReO_3 the enthalpy of formation of $\text{ReO}_3(g)$ by the third law

method would be 72.0 kcal/mole. It seems probable that the true electronic partition function for $\text{ReO}_3(\text{g})$ is not negligible and may well be 5 eu or more. Other sources of error are changes in the fragmentation pattern of Re_2O_7 and in electron multiplier gain from day to day and over long periods of time. A 5% change in the ratio of ReO_3^+ to Re_2O_7^+ from one end of our temperature range to the other would cause a change of 2.5 kcal in the heat of formation calculated for $\text{ReO}_3(\text{g})$ by the second law method. A 5% change in the ratio of Zn^+ to ReO_3^+ would cause a change of 0.5 kcal calculated by the third law method.

Cross sections assumed for the ions produced from the zinc oxide rhenium reaction could be in error by a factor of 2 to 3. If such errors were additive, they would produce a 4.4 to 5.4 kcal error in the third law enthalpy. The only previous equilibrium data on ReO_3 is that summarized in a company report by Norman et al.⁵ Two different mass spectrometers that were employed in that work yielded two divergent second law results, $\Delta H_f(1500) = -76.6$ and -91.5 kcal/mole, for the formation of $\text{ReO}_3(\text{g})$. The various calculated values of ΔH_f for $\text{ReO}_3(\text{g})$ at 298°K are summarized in Table XII.

Calibration of pressure measurements by use of material with known vapor pressures gives support to our second law pressure determinations. Because of the uncertainty in the electronic structure of $\text{ReO}_3(\text{g})$ and the lack of cross section data, less confidence should be placed in the third law heat data. A recommended value may be obtained by giving the second law heat from the zinc oxide experiments twice the weight of the other second law measurement. Greater weight is placed on the zinc oxide rhenium data than was the magnesium oxide rhenium data mainly because the temperature dependence obtained using thermocouples should be

more reliable than these obtained with an optical pyrometer. The result is ΔH_{298}° of -67.0 ± 3.5 . For $\text{Re}_2\text{O}_6(\text{g})$, the second law value is again preferred, but because it is highly sensitive to uncertainties in the large correction for contribution of fragmentation of Re_2O_7^+ to the Re_2O_6^+ ion intensities, the uncertainty must be placed high and the value -209 ± 20 kcal is recommended.

In view of the similarity of the slopes of ReO_3^+ , ReO_2^+ and ReO^+ , the maximum ReO^+ and ReO_2^+ intensities arising from simple ionization can be set at 1/10 of the total ReO^+ and ReO_2^+ ion currents. Pressure independent equilibria can be used with entropies for $\text{WO}(\text{g})$ and $\text{WO}_2(\text{g})$ from JANAF.¹⁵ and with the heat of formation of $\text{ReO}_3(\text{g})$ to establish reliable maximum dissociation energies of $\text{ReO}(\text{g})$ and $\text{ReO}_2(\text{g})$. A maximum value of 279 kcal/mole for ReO_2 is in accord with the value estimated by Brewer.²⁵ For $\text{ReO}(\text{g})$, the upper limit is 155 kcal/mole, which is higher than the average bond energy of $\text{ReO}_3(\text{g})$, (143.9 kcal/bond).

The ionization efficiency curves of ReO_3^+ from Re_2O_7 vaporization and from the zinc oxide rhenium reaction show no distinct break or foot in either case. Since a priori, a 4.0 eV difference in appearance potentials would be expected to cause a change in slopes of the ionization efficiency curve for ReO_3^+ , the ionization efficiency data seems at first anomalous. However, the absence of a change in slope can be readily understood.

It is well known that even the ionization efficiency curve for an atom exhibits a curved foot extending over a few electron volts because the thermal energy spread of the ionizing electrons is usually about 1-2 eV.² The ionization efficiency curve for Zn^+ is shown in Fig. 7. Also shown is the Zn^+ curve shifted four electron volts towards higher energy.

Addition of these curves should give a reasonable approximation of the case in which 50% of the current arises from simple ionization and 50% arise from fragmentation with an appearance potential 4.0 eV higher. The sum of these curves shown in the Fig. 8 is like the ReO_3^+ curves in showing no changes in shape.

It is obvious from Fig. 8 that a curve obtained with the spread in electron energies that characterizes our apparatus would have to have contributions from two processes with appearance potentials that differ by more than 4 eV in order to show an unambiguous linear foot.

The weight loss experiments prove that $\text{Re}_2\text{O}_7(\text{s})$ disproportionates to a small extent and provide new, accurate thermochemical data on the disproportionation reaction.

The present work gives a very reliable value for the enthalpy of the reaction

because an error of 2 orders of magnitude in the calculated oxygen pressure would only result in an error of 2.0 kcal in the heat of reaction. The estimated error in the oxygen pressure calculation is actually fifty times less.

Reported data for the heats of formation of $\text{ReO}_3(\text{s})$ and $\text{Re}_2\text{O}_7(\text{s})$ are shown in Table XIII. Literature values for the heat of formation of $\text{ReO}_3(\text{s})$ are grouped evenly at the two values -146.0 kcal/mole and -140.7 kcal/mole. Since the $\text{Re}_2\text{O}_7(\text{s})$ values are more in agreement, the average value of -298.1 kcal/mole is chosen to be the most reliable and our heat for reaction three, 13.2 kcal, is used to calculate a recommended value of -142.5 kcal/mole for the heat of formation of $\text{ReO}_3(\text{s})$.

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TABLE I. Average intensities of major ions observed in the vapor from Re_2O_7 solid relative to $\text{Re}_2\text{O}_7^+ = 1000$ at 70 eV.

Ion	Intensity	Standard Deviation
Re_2O_7^+	1000	-
Re_2O_6^+	90.7	1.8
Re_2O_5^+	17.4	.4
ReO_3^+	276	10.9
ReO_2^+	154	9.0

TABLE II. Appearance potentials for rhenium-oxygen ionic species in eV.

Ionic Species	This work Re ₂ O ₇ (s) 457°K	Battles at al. Re + Re ₂ O 411°C
Re ₂ O ₇ ⁺	12.7 ± .2	13.0
Re ₂ O ₆ ⁺	16.2 ± .5	16.0
Re ₂ O ₅ ⁺	17.5 ± .2	17.0
ReO ₃ ⁺	16.2 ± .5	~20
ReO ₂ ⁺	21.9 ± 1.0	~20

TABLE III. Debye-Sherrer X-ray Pattern of This Work Compared to the Pattern Reported in the Literature.¹¹

<u>Line</u>	<u>This Work</u>		<u>K. Meisel¹¹</u>	
	<u>d-spacing</u>	<u>Intensity</u>	<u>d-spacing</u>	<u>Intensity</u>
1	5.323		-	
2	4.833	vw	-	
3	4.151	w	-	
4	3.737	ms	3.751	m
5	3.498	w	-	
6	3.362	vw	-	
7	3.207	w	-	
8	2.934	w	-	
9	2.651	s	2.650	m
10	2.160	m	2.154	vw
11	1.872	ms	1.875	w
12	1.671	s	1.674	ms
13	1.528	ms	1.529	m
14	1.323	m	1.322	w
15	1.247	ms	1.246	ms
16	1.1843	m	1.1812	w
17	1.1279	m	1.1262	w
18	1.0795	m	1.0781	vw

TABLE IV. Data for Weight-Loss Experiments on $\text{Re}_2\text{O}_7(\text{s})$.

	<u>Expt. 1</u>	<u>Expt. 2</u>	<u>Expt. 3</u>	<u>Expt. 4</u>	<u>Expt. 5</u>
Temperature ($^{\circ}\text{K}$)	430.9	424.9	424.6	423.7	429.4
Time (sec) *	1.396×10^5	3.410×10^5	5.081×10^4	2.915×10^5	1.805×10^4
Initial Weight (g.)	.54004	.78405	.55729	.09147	.31128
Residue (ReO_3)(g)	.01041	.00607	.00904	.00410	.00748
Orifice Area (cm^2)	1.046×10^{-2}	1.088×10^{-2}	3.40×10^{-2}	1.075×10^{-3}	3.40×10^{-2}
Orifices	2	2	1	1	1
Clausing Factor	.620, .631	.638, .620	.980	.935	.980
Pressure of $\text{Re}_2\text{O}_7(\text{g})$ *(Atm)	1.233×10^{-5}	7.031×10^{-6}	6.839×10^{-6}	6.281×10^{-6}	1.074×10^{-5}
Pressure of $\text{O}_2(\text{g})$ (Atm)	3.22×10^{-8}	7.29×10^{-9}	1.50×10^{-8}	4.05×10^{-8}	3.395×10^{-8}

* The pressure of $\text{Re}_2\text{O}_7(\text{g})$ from previous experiments was used to calculate the time for the cell to exhaust.

TABLE V. Values of ΔH_{298}° for the reaction $\text{Re}_2\text{O}_7(\text{g}) = 2\text{ReO}_3(\text{s}) + 1/2\text{O}_2(\text{g})$ from weight loss data.

Temperature ($^\circ\text{k}$)	$\Delta F_T^\circ(\text{kcal})$	orifice area (cm^2)	$\frac{-(\Delta F_T^\circ - \Delta H_{298}^\circ)}{T}$	$\Delta H_{298}^\circ(\text{kcal})$
430.9	7.382	.01046	13.409	13.160
424.9	7.909	.01046	13.422	13.612
424.6	7.599	.034	13.423	13.298
423.7	7.164	.001075	13.425	12.852
429.4	7.337	.034	13.412	13.096

TABLE VI. Secondary electron multiplier relative gains of ions of importance in the Re-ZnO experiments and Otvos and Stevenson cross sections for electron impact ionization.

Ion	Relative Gain	Cross Sections
Re_{207}^{484}	1	113
Zn^{64}	.857	16
ReO_3	1.00	54.9
ReO_2	1.00	51.6
Re_{206}^0	.933	110
Re_{205}^0	.93(est.)	107

TABLE VII. Weight loss data for silver calibration.

	<u>Expt. 1</u>	<u>Expt. 2</u>
Temperature ($^{\circ}$ K)	1205 $^{\circ}$	1206 $^{\circ}$
Time (sec)	2.201×10^5	9.24×10^4
Weights loss (g)	0.00275	0.00103
Clausing factor	0.4	0.4
Area (cm^2)	6.425×10^{-4}	6.425×10^{-4}
Pressure (atm)	3.65×10^{-6}	3.26×10^{-6}

TABLE VIII. Average appearance potentials of ions above Re-ZnO mixtures.

Ion	Appearance Potentials (eV)
ReO_2^+	18.0 ± 0.8
ReO_3^+	14.7 ± 0.6
Re_2O_5^+	16.1 ± 0.8
Re_2O_6^+	16.1 ± 0.6
Re_2O_7^+	13.6 ± 0.8

TABLE IX. Average intensities of major ions observed from the vapor from Re-ZnO equilibria at 1200°K relative to $\text{Re}_2\text{O}_7^+ = 1000$.

Ion	Intensity (at 70 eV)	Standard Deviation
Re_2O_7^+	1000	---
$\text{Re}_2\text{O}_6^{+a}$	130.8	12.3
$\text{Re}_2\text{O}_5^{+b}$	23.39	1.71
ReO_3^{+a}	718.1	255.2
ReO_2^{+b}	217.9	52.1
a six measurements		
b three measurements		

TABLE X. Vaporization weight loss data for ZnO-Re mixture experiments.

	1	2	3
Temperature ($^{\circ}$ K)	1245	1177	1187
Time (sec)	4.00×10^4	1.601×10^5	1.751×10^5
Weight loss	.03361	.02653	.03582
Clausing factor	.4	.4	.4
Area (cm^2)	6.425×10^{-4}	6.425×10^{-4}	6.425×10^{-4}
True Partial Pressures (atm)			
(1) Zn(g)	1.55×10^{-4}	3.02×10^{-5}	4.59×10^{-5}
(2) $\text{Re}_2\text{O}_7(\text{g})$	9.15×10^{-6}	1.68×10^{-6}	2.66×10^{-6}
(3) $\text{ReO}_3(\text{g})$	1.65×10^{-6}	5.58×10^{-7}	1.235×10^{-6}
(4) $\text{Re}_2\text{O}_6(\text{g})$	9.86×10^{-8}	7.05×10^{-8}	1.60×10^{-7}
Equilibrium Constants			
$\text{Re}(\text{s}) + 3\text{ZnO}(\text{s})$	6.146×10^{-18}	1.537×10^{-20}	1.194×10^{-19}
$\text{ReO}_3(\text{g}) + 3\text{Zn}(\text{g})$			
$2\text{Re}(\text{s}) + 6\text{ZnO}(\text{s})$	1.368×10^{-30}	5.347×10^{-35}	1.496×10^{-33}
$\text{Re}_2\text{O}_6(\text{g}) + 6\text{Zn}(\text{g})$			
$2\text{Re}(\text{s}) + 7\text{ZnO}(\text{s})$	1.967×10^{-32}	3.849×10^{-38}	1.142×10^{-36}
$\text{Re}_2\text{O}_6(\text{g}) + 7\text{Zn}(\text{g})$			

TABLE XI. Enthalpies of reaction and entropies of reaction calculated from mass spectrometer measurements for the Re-ZnO reactions (Corrected to agree with the silver enthalpy measurements and weight loss results) Quoted errors are standard deviations from the least squares fit.

Equilibrium	Experiment	Midpoint temperature(°K)	ΔH_T°
$\text{Re(s)} + 3\text{ZnO(s)} \rightarrow$ $\text{ReO}_3\text{(g)} + 3\text{Zn(g)}$	1(13 points)	1155	263.7±3.7
	2(11 points)	1145	266.7±2.4
	3(13 points)	1128	264.7±3.0
	4(12 points)	1189	275.9±2.6
	5 (9 points)	1152	271.2±2.1
$\Delta S_{\text{Ave}}^\circ = 137.8 \pm 3.0 \text{ eu}$		$\Delta H_{\text{Ave}}^\circ = 268.2 \pm 3.0 \text{ kcal}$	
$2\text{Re(s)} + 6\text{ZnO(g)} \rightarrow$ $\text{Re}_2\text{O}_6\text{(g)} + 6\text{Zn(g)}$	1(13 points)	1155	452.0±6.8
	2(11 points)	1145	458.0±5.8
	3(12 points)	1128	453.5±7.0
	4(15 points)	1175	465.3±6.2
$\Delta S_{\text{Ave}}^\circ = 233.0 \pm 8.0 \text{ eu}$		$\Delta H_{\text{Ave}}^\circ = 457.9 \pm 6.0 \text{ kcal}$	
$2\text{Re(s)} + 7\text{ZnO(s)} \rightarrow$ $\text{Re}_2\text{O}_7\text{(g)} + 7\text{Zn(g)}$	1(13 points)	1155	514.4±8.3
	2(11 points)	1145	515.3±4.6
	3(13 points)	1128	516.3±3.9
	4(15 points)	1175	505.0±6.3
	5(10 points)	1152	538.9±9.3
$\Delta S_{\text{Ave}}^\circ = 267.8 \pm 7.8 \text{ eu}$		$\Delta H_{\text{Ave}}^\circ = 516.5 \pm 7.1 \text{ kcal}$	

TABLE XII. Enthalpies of formation for $\text{ReO}_3(\text{g})$ and $\text{Re}_2\text{O}_6(\text{g})$.

Molecule	Method of Calculation	Temperature K	ΔH_f (kcal/mol $\hat{e}$)		
			Norman et al.	This work ZnO+Re	This work MgO+Re
ReO_3	Second law	298	-75.8, -90.6 ^a	-66.6 $\pm$ 3.0	-67.7
	Third law	298	-62.7 ^a	-74.6 $\pm$ 5.0	$\pm$ 5.0
Re_2O_6	Second law	298		-200.7 $\pm$ 6.0	
	Third law	298		-216.8 $\pm$ 7.0	

^a Calculated from the data of Norman et al. using the same auxillary data used for this work.

TABLE XIII. Reported heats of formation at 298°K for $\text{Re}_2\text{O}_7(\text{s})$ and $\text{ReO}_3(\text{s})$.

Compound	ΔH_{f298} kcal/mole	Method	Investigation
ReO_3	-140.8 ± 0.9	solution calorimetry bomb calorimetry	King et al. ²⁶
	-146.0 ± 3.0		Boyd et al. ²⁷
	-83.0		Roth and Becker ²⁸
	$-146.1 \pm .8$	cell potential	King and Cobble ¹⁴
	-140.7 ± 2.0	mass spectro- meter	Battles et al. ⁴
Re_2O_7	-301.9 ± 1.8	solution calorimetry bomb calorimetry	King et al. ²⁶
	-295.0 ± 2.0		Boyd et al. ²⁷
	-297.5		Roth and Becker ²⁸

XBL 706-3065

Figure 1. Vaporization data for rhenium heptoxide.

XBL 707-3320

Figure 2. Ionization efficiency data for ReO_3 at two temperatures up to 25 eV.

XBL 707-3321

Figure 3. Equilibrium constant vs. reciprocal temperature for the equilibrium $\text{Re(s)} + 3 \text{ ZnO(s)} \rightarrow \text{ReO}_3\text{(g)} + 3 \text{ Zn(g)}$. To bring the pressures calculated by zinc calibration into coincidence with weight-loss measurements, the pressures were multiplied by the following factors: $\diamond 0.484$, $\triangle 1.12$, $\nabla 1.17$, $\square 5.48$, $\circ 5.48$.

XBL 707-3319

Figure 4. Equilibrium constant vs reciprocal temperature for the equilibrium $2\text{Re(s)} + 6\text{ZnO(s)} \rightarrow \text{Re}_2\text{O}_6\text{(g)} + 6\text{Zn(g)}$. To bring the pressures calculated by zinc calibration into coincidence with weight-loss measurements. The pressures were multiplied by the following factors: $\diamond 0.484$, $\triangle 1.12$, $\square 5.48$, $\circ 5.48$.

XBL 707 - 3322

Figure 5. Equilibrium constant vs reciprocal temperature for the equilibrium $2\text{Re(s)} + 7\text{ZnO(s)} \rightarrow \text{Re}_2\text{O}_7\text{(g)} + 7\text{Zn(g)}$. To bring the pressures calculated by zinc calibration into coincidence with weight-loss measurements, The pressures were multiplied by the following factors: ◇ 0.484, △ 1.12, ▽ 1.17, □ 5.48, ○ 0.548.

Figure 6. Ion intensity-temperature product vs reciprocal temperature for the equilibrium $3\text{MgO(s)} + \text{Re(s)} \rightarrow \text{ReO}_3\text{(g)} + 3\text{Mg(g)}$
 $\square$ Run 1, $\circ$ Run 2.

Figure 7. Plots of ionization efficiency curves for Zn^+ with one curve shifted 4 eV towards higher energy. XBL 707-1475

XBL 707-1474

Figure 8. Sum of ionization efficiency curves for Zn^{+} from Fig. 7.

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