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MASS SPECTROMETRIC STUDIES OF GASEOUS OXIDES OF RHENIUM

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ABSTRACT

Effusion cell mass spectrometry has been employed to study vapor species of the rhenium-oxygen system. The equilibrium partial pressure of \( \text{Re}_2\text{O}_7(g) \) above solid rhenium heptoxide at 327 to \( 463^\circ\text{K} \) is given by

\[
\log P_{\text{Re}_2\text{O}_7} = -(7.44 \pm 0.08) \frac{10^3}{T} + (12.35 \pm 0.21)
\]

where the pressure is in atmospheres. The enthalpy of sublimation at \( 430^\circ\text{K} \) is \( 34.0 \pm 2 \text{ kcal/mole} \). The only other measurable vapor species is a much lower pressure of oxygen, which is produced by the reaction

\[
\text{Re}_2\text{O}_7(s) \rightarrow 2 \text{ReO}_3(s) + \frac{1}{2} \text{O}_2(g).
\]

Weight loss measurements yield \(+13.2 \pm 2.0 \text{ kcal}\) for the enthalpy of the reaction at \( 298^\circ\text{K} \). The reaction of rhenium with zinc oxide at \( 1047^\circ\text{K}\) to \( 1267^\circ\text{K} \) produces \( \text{Re}_2\text{O}_7(g), \text{ReO}_3(g) \) and possibly \( \text{Re}_2\text{O}_6(g) \). Reaction of rhenium with magnesium oxide at \( 1770^\circ\text{K} \) to \( 2143^\circ\text{K} \) produces principally \( \text{ReO}_3(g) \). The enthalpy of formation of \( \text{ReO}_3(g) \) is \(-67.0 \pm 4 \text{ kcal per mole}\) at \( 298^\circ\text{K} \) and that of \( \text{Re}_2\text{O}_6(g) \) is \( \geq -212 \pm 20 \text{ kcal per mole} \) at \( 298^\circ\text{K} \).
Re$_2$O$_5$(g), ReO$_2$(g) and ReO(g) are not present at measurable concentrations under any of the conditions of study. The heats of formation ReO(g) and ReO$_2$(g) are more positive than -10 kcal and +48 kcal per mole respectively.
INTRODUCTION

The vapor pressure for the reaction \( \text{Re}_2\text{O}_7(s) + \text{Re}_2\text{O}_7(g) \) was measured by Ogawa,\(^1\) by Smith, Line and Bell\(^2\) and more recently by Clemmer, Muller, and Stocke.\(^3\) A mass spectrometer investigation of vapors from the solids \( \text{ReO}_3 \) and \( \text{ReO}_2 \) was first made by Semenov and Ovchinnikov,\(^4\) who reported that both \( \text{ReO}_3(g) \) and \( \text{Re}_2\text{O}_7(g) \) are important species in vaporization of both phases. However, Battles, Gunderson and Edwards\(^5\) showed that \( \text{ReO}_3(s) \) and \( \text{ReO}_2(s) \) do not vaporize congruently as reported by Semenov and Ovchinnikov\(^4\) and that \( \text{Re}_2\text{O}_7(g) \) was the only major vapor species over the solid phase mixtures \( \text{ReO}_3-\text{ReO}_2 \) and \( \text{ReO}_2-\text{Re} \). Norman, Winchell and Staley\(^6\) were able to study the reaction of rhenium metal with oxygen to form \( \text{ReO}_3(g) \) but obtained conflicting measurements of its stability.

This paper reports mass spectrometer investigations of vaporization of \( \text{Re}_2\text{O}_7-\text{ReO}_3 \) solid mixtures, of \( \text{Re-ZnO} \) solid mixtures, and of \( \text{Re-MgO} \) solid mixtures which were undertaken to obtain, if possible, more precise data for \( \text{ReO}_3(g) \) and to determine if additional gaseous rhenium oxides could be identified and studied. In the course of the work it was discovered that solid \( \text{Re}_2\text{O}_7 \) does not vaporize congruently in vacuum but has a low partial pressure of oxygen. This partial pressure was determined and was used to reconcile discordant measurements of the heats of formation of solid \( \text{ReO}_3 \) and solid \( \text{Re}_2\text{O}_7 \).
RHENIUM HEPTOXIDE VAPORIZATION

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. had Mg as the only impurity detectable by spectroscopic analysis.

The sample was resistively heated by nichrome wire wound closely around an anodized aluminum effusion cell. The interior of the cell was gold plated and a gold lid and liner were installed to prevent any contact of the rhenium heptoxide sample with the aluminum.

The sample color changed after prolonged heating, which suggested that some reaction other than simple congruent sublimation was occurring. X-ray diffraction measurements demonstrated that a residue of ReO₃(s) remained after long heating of a rhenium heptoxide sample.

Samples of solid Re₂O₇ that initially weighed about 0.5 g were heated to constant weight at about 430⁰K in a separate vacuum system capable of ~2x10⁻⁶ torr using the effusion cell and liner from the mass spectrometric experiments. Heating times of 60 to 150 hours were required. Spectroscopically detectable impurities in the ReO₃(s) residue were Mg, Si, and Fe, all present at less than 2% of the Re concentration.

Bombardment of the vapor from the Re₂O₇-ReO₃ solid mixtures by 70 eV electrons produced Re₂O₇⁺, Re₂O₆⁺, Re₂O₅⁺, ReO₃⁺, and ReO₂⁺, which were each measured seven or more times over a seven day period while the rhenium heptoxide was held at about 404⁰K. Appearance potentials were measured by the method of extrapolated differences with the mercury ion intensity 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 ions found in Re₂O₇(s) vaporization to arise from an Re₂O₇(g) parent molecule. (See discussion section.)

The intensity of the Re₂O₇⁺ ion 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 a 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°. Two five 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° of each other. The thermocouples were calibrated by determination of the melting point of 99.999% indium, 429.3 K.⁷ They gave melting points of 430.0°K and 430.3°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 points were taken in random order over the temperature range 427 to 512°K. A least square enthalpy of 26.72 ± .52 kcal/mole (where the quoted error is the standard deviation), was calculated from the data. Hultgren's⁷ selected value at 469°K is 26.41 ± .15 kcal/mole.
Results

The steady state relative intensities of the major species observed over Re$_2$O$_7^+$ are shown in the first two columns of Table I, which also records measured appearance potentials. Intensities of Re$_2$O$_6^+$ and Re$_2$O$_5^+$ changed little relative to Re$_2$O$_7^+$ during the initial days of vaporization, but intensities of ReO$_2^+$ decreased some 27% and of ReO$_3^+$ decreased about 26%. These changes are attributed to gradual reduction in contamination by HReO$_4$, from which ReO$_3^+$ and ReO$_2^+$ would arise through a fragmentation process.

Data for the steady state Re$_2$O$_7^+$ ion are plotted in Fig. 1. Also shown are the total pressure measurements of Glemser et al.$^3$ and Smith et al.$^2$

The least squares fit of log [T I$_{Re_2O_7^+}$] vs $\frac{1}{T}$ for each run was made to coincide at the average pressure of Glemser et al. and Smith et al. at 433.3$^\circ$K (Fig. 1). Enthalpies calculated from temperature dependence of intensities for the three runs were 33.25 ± .72 kcal/mole, 35.30 ± .15 kcal/mole, and 36.45 ± .92 kcal/mole. The least squares fit of all the data normalized to this point yielded an enthalpy of sublimation of 34.0 ± 0.4 kcal/mole and an entropy of sublimation of 56.0 ± 1.0 eu/mole.

The vapor pressure of Re$_2$O$_7$ from 327$^\circ$K to 463$^\circ$K is given by the equation

$$\log P_{atm} = - (7.44 ± 0.08) \frac{10^3}{T} + (12.35 ± 0.21)$$  (1)

where the quoted errors are the standard deviations from the least squares fit.
The weight loss as $\text{Re}_2\text{O}_7(g)$ per unit time calculated from (1) by means of the Hertz-Knudsen-Langmuir equation \(^8\) was extrapolated to the time when the $\text{Re}_2\text{O}_7(s)$ was all vaporized or decomposed to obtain the time period during which the reaction

$$\text{Re}_2\text{O}_7(s) \rightarrow 2 \text{ReO}_3(s) \pm 1/2 \text{O}_2$$  \hspace{1cm} (2)

took place. This time of reaction and the weight of $\text{ReO}_3(s)$ remaining permitted calculation of the pressure of the oxygen which had effused from the cell. These oxygen pressures are plotted in Fig. 1 and Gibbs free energies for reaction (2) calculated from them are given in Table II.

It was necessary to estimate the free energy functions for both $\text{Re}_2\text{O}_7(s)$ and $\text{ReO}_3(s)$ to obtain the Third Law Heat at 298\(^0\)K for reaction (2). The heat capacity for $\text{Re}_2\text{O}_7(s)$ was estimated to be linear from the value given by Busey\(^9\) at 298\(^0\)K to the melting point where the $C_p$ was estimated to be 7.0 cal/deg-atom.\(^10\) This gave $C_p = 14.55 + 8.47 \times 10^{-2}T$. King\(^10\) and Cobble\(^11\) have reported for $\text{ReO}_3(s)$ $S_{298} = 19.3$ eu/mole. The heat contents and entropy increases above 298\(^0\)K for $\text{ReO}_3(s)$ were assumed to be the same as the values reported for $\text{WO}_3(s)$ in JANAF,\(^12\) and JANAF data were used for $\text{O}_2(g)$.

**ZINC OXIDE-RHENIUM EQUILIBRIUM**

**Experimental**

Reagent grade zinc oxide supplied by Baker and Adamson, which was used in this part of the study, showed 0.15% Mn, 0.06% Si and 0.025% Ca as the principal spectroscopically detectable impurities. The rhenium powder obtained from the Department of Chemistry, University of Tennessee,
showed .015% Si as the principal impurity.

Mass spectrometer experiments were performed in a molybdenum or tantalum outer cell with either an alumina cell liner or a rhenium liner. A machined alumina cell was constructed for weight loss experiments. Orifice areas were smaller by a factor of $\sim 10$ than those used by Anthrop and Searcy$^{13}$ to obtain equilibrium data in zinc oxide vaporization.

Heating at lower temperatures was by radiation from 2 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 silver in the range 1051 to 1225 K. Fourteen measurements made in random order yielded a least squares enthalpy of sublimation $64.48 \pm 0.44$ kcal/mole at 1138 K. The value interpolated from Hultgren's$^7$ tabulation is $66.49 \pm 0.20$ kcal.

Otvos and Stevenson$^{14}$ cross sections for electron impact ionization were used with the assumption that atomic cross sections are additive. Measured electron multiplier gains relative to Re$_2$O$_7^{48}$ = 1 were:

$\text{Zn}^{64} = 0.86$; $\text{ReO}_3 = 1.0$; $\text{ReO}_2 = 1.0$ and $\text{Re}_2\text{O}_6 = 0.9$. The relative gain for Re$_2$O$_5$ was assumed to be 0.9.

The intensity of each ion produced with 70 eV electrons was followed as a function of temperature in five separate 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 Re-ZnO mixture. Measurement of the vapor pressure of zinc at low temperature provided a direct determination of the proportionality constant between $I^+_T$ and pressure for Zn(g). Several Zn$^+$ intensities were measured, then the Zn was exhausted and the rhenium-zinc oxide equilibrium was measured. In addition, weight loss experiments were performed at constant temperature. The ion intensities of Zn$^+$, Re$_2$O$_7^+$, ReO$_3^+$, and Re$_2$O$_6^+$ were measured several times during a run, then averaged and corrected for fragmentation in order to calculate equilibrium constants for the following reactions:

$$Re(s) + 3ZnO(s) \rightarrow ReO_3(g) + 3Zn(g)$$  \hspace{1cm} (3)  \\
$$2Re(s) + 6ZnO(s) \rightarrow Re_2O_6(g) + 6Zn(g)$$  \hspace{1cm} (4)  \\
$$2Re(s) + 7ZnO(s) \rightarrow Re_2O_7(g) + 7Zn(g)$$  \hspace{1cm} (5)

Losses during heating and cooling were negligible.

To check the accuracy of the weight loss experiments, two weight loss measurements were made on silver. Measured silver pressures were found to be approximately 1.7 times higher than the pressures selected by Hultgren. The measured total pressure in ZnO-Re weight loss experiments was reduced by this factor to correct for systematic errors.

Average appearance potentials measured for rhenium oxide ions produced from the vapor above ZnO-Re mixtures are given in the last column of Table I. One set of measurements was made using background mercury
as a standard, another used Zn\(^+\) from the reduction of zinc oxide to zinc vapor.

A cell exhaustion experiment was made to determine if the Re\(_2\)O\(_5\)\(^+\) was all produced by fragmentation of Re\(_2\)O\(_7\)(g) or if some arose from ionization of Re\(_2\)O\(_6\)(g). If Re\(_2\)O\(_6\)(g) is present in significant amounts in the vapor above zinc oxide-rhenium mixtures, the Re\(_2\)O\(_6\)\(^+\) peak should decrease more slowly than the Re\(_2\)O\(_7\)\(^+\) peak. For this experiment, excess rhenium powder was mixed with a very small portion of zinc oxide powder. The mixture was heated to about 1186\(^\circ\) and held until the intensities began to drop. The intensities of Re\(_2\)O\(_7\)\(^+\) and Re\(_2\)O\(_6\)\(^+\) 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\(^\circ\) causing the intensities to increase. The intensity of each ion was again followed at constant temperature until the Re\(_2\)O\(_6\)\(^+\) intensity had dropped to a value which was difficult to measure in a time span of one min. This process was repeated until at about 1450\(^\circ\)K the Re\(_2\)O\(_6\)\(^+\) ion intensity became too small for accurate measurements.

**Results**

The average of several separate measurements at 1200\(^\circ\)K of the intensities of the major ions above Re-ZnO mixtures are given in Table I. The intensities of all the lighter ions are significantly increased relative to Re\(_2\)O\(_7\)\(^+\) and the appearance potentials measured for ReO\(_3\)\(^+\) and ReO\(_2\)\(^+\) are distinctly lower than values found from Re\(_2\)O\(_7\)(s) vaporization (Table I).

Each temperature increase in the cell exhaustion experiments reduced the oxygen activity further and constant temperature Re\(_2\)O\(_6\)\(^+\)/Re\(_2\)O\(_7\)\(^+\)
ratios measured over a period of time showed steady decreases. The ratio of $\text{Re}_2\text{O}_6^+$ to $\text{Re}_2\text{O}_7^+$ during the initial decline at $1186^\circ\text{K}$ was 0.106. On increasing the temperature to $1235^\circ\text{K}$, $1298^\circ\text{K}$, $1353^\circ\text{K}$ and $1407^\circ\text{K}$ this ratio increased to 0.107, then 0.126, 0.133 and 0.139. At $1436^\circ\text{K}$, the $\text{Re}_2\text{O}_6^+/\text{Re}_2\text{O}_7^+$ ratio was found to be $0.154$ 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 $\text{Re}_2\text{O}_7^+$: $58.25 \pm 0.68$, $\text{Re}_2\text{O}_6^+$: $59.53 \pm 0.92$, and $\text{ReO}_3^+$: $64.30 \pm 0.66$, all in kcal per mole.

These results, plus comparison of ion intensities obtained under greater and less strongly reducing conditions (see discussion) demonstrated that the important neutral precursors of the rhenium-containing ions in the rhenium metal-zinc oxide experiments were $\text{Re}_2\text{O}_7(g)$, $\text{ReO}_3(g)$ and possibly $\text{Re}_2\text{O}_6(g)$. 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 $\text{Re}_2\text{O}_7$ (Table I) was subtracted from the total ion current for that ion. The currents were then multiplied by temperature and divided by cross-sections to obtain pressure values.

The results of the weight loss experiments on rhenium-zinc oxide mixtures are shown in Table III and the equilibrium constants are plotted in Fig. 2 for the reaction $\text{Re(s)} + 3\text{ZnO(s)} = \text{ReO (g)} + 3\text{Zn(g)}$ for comparison with results of the temperature variation experiments. When the cross section measured for zinc by vaporization of zinc metal was used, 2 of the 5 runs gave calculated zinc pressures about a factor of 5 lower than those measured in the weight loss experiments. Only small amounts
of zinc were used and equilibrium zinc pressures probably were not developed in the cells during the calibration periods of these two runs. Each mass spectrometer run was normalized, therefore, to agree with the zinc loss of the weight loss experiments.

The enthalpies of equilibrium constant measurements for the reaction

\[ 2\text{Re}(s) + 7 \text{ZnO}(s) = \text{Re}_2\text{O}_7(g) + 7 \text{Zn}(g) \]  

(6)

were corrected for the error in temperature dependence of pressures found for silver. The correction for reaction (6) is \(+16.0 \pm 3.5\) kcal/mole, yielding an average enthalpy of 516.5 kcal/mole at 1156°C. An internal check on the corrected enthalpy can be made since the heat of formation of Re\(_2\)O\(_7\)(g) can be calculated from the heat of vaporization of Re\(_2\)O\(_7\)(g) and the heat of formation of Re\(_2\)O\(_7\)(s). When temperature corrections are made using data from Kelly\(^{15}\) for Re(s), ZnO(s), and Zn(g) and the approximation that the heat content for Re\(_2\)O\(_7\)(g) is that given by JANAF\(^{12}\) for W\(_2\)O\(_6\)(g) the heat for reaction (6) is calculated to be 521.3 ± 3.0 kcal, in fair agreement with the corrected value of 516.5 kcal.

Enthalpies and average entropies calculated from the equilibrium constant measurements for the three equilibria, after correction of the error in the enthalpy of sublimation, are given in Table IV. 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 heat of formation of ReO₃(g) and Re₂O₆(g) at 298°K were calculated by the second and third law methods. (Table V). For ReO₃(g), estimated free energy function and heat content values were available.¹⁵ For Re₂O₆, the thermochemical values given by JANAF¹² for W₂O₆ 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 Re(s) and O₂(g) were taken from Kelly,¹⁵ and data for Zn(g) from Hultgren.⁷

THE MAGNESIUM OXIDE-RHENIUM EQUILIBRIUM

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 measurements, after vaporization, showed no evidence of phases other than magnesium oxide and rhenium.

A tungsten outer cell and lid with a 0.08 cm orifice surrounded a rhenium cell liner. Three filaments were used, with the third being placed slightly above center to ensure that the lid was hotter than the cell 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 Berkeley Laboratory meter shop. To obtain a correction for temperature-dependent errors, the second law enthalpy of sublimation of lanthanum metal was measured in the temperature range 1794°K to 2103°K.
Ten points yielded $\Delta H_{1950} = 93.4 \pm 1.7$ kcal/mole, in only fair agreement with the value of $99.7 \pm 1.0$ kcal/mole interpolated from Hultgren's tabulation.

Two temperature variation experiments were conducted in a manner similar to those used for zinc oxide and rhenium using 70 eV electrons. Appearance potentials were measured using background mercury as a standard for the extrapolated differences method.

**Results**

Ions identified as $\text{Mg}^+$, $\text{ReO}_3^+$, $\text{ReO}_2^+$, and $\text{ReO}^+$ were observed. Relative intensities at 2080°K and appearance potentials are included in Table I.

Both $\text{ReO}^+$ and $\text{ReO}_2^+$ arise primarily from dissociative ionization of $\text{ReO}_3(g)$ (see discussion), and quantitative data can be derived only from the $\text{ReO}_3^+$ measurements. The equilibrium constant for the reaction

$$\text{Re(s)} + 3\text{MgO(s)} = \text{ReO}_3(g) + 3\text{Mg}(g)$$

is plotted in Fig. 3. Least squares analysis yielded $425.9 \pm 5.1$ kcal/mole and $429.1 \pm 5.7$ kcal/mole for the heat of reaction. The average of these enthalpies is $452.7 \pm 5$ kcal/mole after the measured temperature dependence of the cell is corrected to make the measured second law enthalpy of sublimation of lanthanum metal agree with the accepted value. When this average for Eq. (7) is combined with thermochemical enthalpy data for MgO and Mg$(g)$, the heat of formation of ReO$_3(g)$ at 1980°K is calculated to be $-69.6 \pm 5$ kcal/mole.
DISCUSSION

In order to calculate partial pressures from mass spectrometry intensity measurements such as obtained in this study, it is necessary to establish the formulas of the vapor molecules from which the observed ions are produced. These neutral molecules may include species of higher molecular weights than any of the ions observed in the mass spectrum for the vapor. For the rhenium oxygen system, however, significant concentrations of molecules of higher oxygen to rhenium atomic ratio than 7/2 are very unlikely on chemical grounds. Polymers of Re\textsubscript{2}O\textsubscript{7}(g) are possible vapor species, but such polymers, if present at compositions comparable with the monomer, would almost certainly yield measurable concentrations of ions of greater mass than Re\textsubscript{2}O\textsubscript{7}\textsuperscript{+}. Since ions of higher mass than Re\textsubscript{2}O\textsubscript{7} were not observed, it is virtually certain that all the Re\textsubscript{2}O\textsubscript{7} ions were produced by simple ionization of Re\textsubscript{2}O\textsubscript{7}(g). The data collected for Re\textsubscript{2}O\textsubscript{7} and ions of lower masses under three distinctly different sets of experimental conditions can be used to determine the parent molecules for these other ions.

When rhenium metal was heated with magnesium oxide at 2080°K, none of the ions Re\textsubscript{2}O\textsubscript{7}\textsuperscript{+}, Re\textsubscript{2}O\textsubscript{6}\textsuperscript{+}, or Re\textsubscript{2}O\textsubscript{5}\textsuperscript{+}, which are important in the Re\textsubscript{2}O\textsubscript{7}(g) mass spectrum, was observed at intensities as high as 0.1% that observed for ReO\textsubscript{3}. The ReO\textsubscript{3}, ReO\textsubscript{2}, and ReO\textsuperscript{+} ions which were observed, therefore, must have as parents a molecule no more complex than ReO\textsubscript{3}. The apparent enthalpies of reaction of rhenium with magnesium oxide to produce the parent of the three ions were 108.9 ± 2.6 kcal per mole for ReO\textsubscript{3}+, 113.9 ± 2.9 for ReO\textsubscript{2}+, and 115.4 ± 2.9, where the uncertainties are standard deviations. These similar enthalpy values constitute strong
evidence that the principal parent for all three ions is ReO$_3^+$. The measured appearance potentials support this conclusion because the appearance potential found for ReO$_3^+$ is about the same as found for Re$_2$O$_7^+$, which must be formed by simple ionization of Re$_2$O$_7^+$, while the appearance potential of ReO$_2^+$ is two volts higher and that of ReO$^+$ is some five volts higher than that found in the same experiment for ReO$_3^+$. It should be remarked that the method of extrapolated differences that was used in obtaining appearance potentials seemed to give an apparent appearance potential for any ion which has two different parents that is a function of the relative concentrations of the two parents in the vapor. Thus the apparent appearance potentials of ReO$_3^+$ drops from 16 ev when Re$_2$O$_7$ gas is its only important parent to 15 ev when Re$_2$O$_7$ and ReO$_3$ are present in roughly equal concentrations to 12.5 when ReO$_3$ is the only significant parent. The apparent appearance potentials of ReO$_2^+$ show similar variations as the proportions of Re$_2$O$_7$ and ReO$_3$ change. The values measured over Re$_2$O$_7$ are measures of the appearance potentials from fragmentation of Re$_2$O$_7$ and the value for ReO$_3^+$ measured when rhenium was heated with zinc oxide is a measure of the ionization potential of ReO$_3$(g).

A most negative possible value for the heat of formation of ReO$_2$ gas is calculated to be $\geq -10$ kcal per mole and for ReO $\geq 48$ kcal/mole, both at 1980$^\circ$K. These limits are obtained by adding a 5 kcal per mole uncertainty to the heats of formations calculated on the assumption that the ReO$_2^+$ and ReO$^+$ ions have ReO$_2$ and ReO as their respective parents.
When the heats of formation, or limits to heats of formation, which were determined for ReO$_3$, ReO$_2$, and ReO from the rhenium metal reaction with magnesium oxide are used with entropy and heat capacity data estimated to be the same for the gaseous rhenium oxides as for corresponding tungsten oxides, the conclusion that none of these three oxides is an important species in the vapor above a solid ReO$_3$-solid Re$_2$O$_7$ mixture is confirmed.

Above mixtures of rhenium metal with zinc oxide, however, ReO$_3$ gas is present in concentrations comparable to Re$_2$O$_7$ gas. This conclusion is warranted both by the observed increase in ReO$_3$/Re$_2$O$_7$ ratio and by the agreement between the enthalpy of formation of ReO$_3$ calculated from the Re-MgO data with that calculated from the Re-ZnO data after correction for fragmentation of Re$_2$O$_7$.

The observed Re$_2$O$_5^+$ must be essentially all produced by fragmentation of Re$_2$O$_7^+$ since the intensity ratio Re$_2$O$_5^+/Re$_2$O$_7^+$ is not measurably changed by alterations in reaction conditions or temperature and since the appearance potential for Re$_2$O$_5^+$ is relatively high.

The principal parent of Re$_2$O$_6^+$ must be Re$_2$O$_7$ gas even when the ion was produced by heating rhenium metal with zinc oxide. The increase in Re$_2$O$_6^+/Re$_2$O$_7^+$ ratios with temperature and time in the cell exhaustion experiment and the increase in the same ratio when rhenium was heated with zinc oxide over that when the solid ReO$_3$-solid Re$_2$O$_7$ mixture was heated suggest that Re$_2$O$_6^+$ has a second parent, which could only be Re$_2$O$_5$ gas.

The closely similar temperature dependences measured for Re$_2$O$_6^+$ and Re$_2$O$_7^+$ ion intensities in the rhenium metal-zinc oxide heating (the
apparent heat of vaporization for \( \text{Re}_2\text{O}_6^+ \) was 59.5 ± 0.9 kcal/mole and for \( \text{Re}_2\text{O}_7^+ \) was 58.3 ± 0.7) implies, on the other hand, a single common parent, although the result could be coincidentally obtained if \( \text{Re}_2\text{O}_6 \) gas is a significant parent for \( \text{Re}_2\text{O}_6^+ \). A stronger argument against \( \text{Re}_2\text{O}_6 \) gas as a parent for a significant fraction of the observed \( \text{Re}_2\text{O}_6^+ \) ion intensity is the high appearance potential, 16 ev measured for \( \text{Re}_2\text{O}_6^+ \) compared to about 12.5 for \( \text{Re}_2\text{O}_7^+ \) and \( \text{ReO}_3^+ \) when these ions are produced from \( \text{Re}_2\text{O}_7(g) \) and \( \text{ReO}_3(g) \) respectively. In light of the conflicting data, we can only calculate a maximum stability for \( \text{Re}_2\text{O}_6 \) gas.

Values calculated for the heat of formation of \( \text{ReO}_3 \) from data of three different investigations are listed in Table V. All values are calculated with the assumption that the free energy functions for \( \text{ReO}_3 \) gas are the same as JANAF free energy functions for \( \text{WO}_3 \). In addition to the results of Norman et al.\(^6\) and of the present investigation, a value calculated by Franklin and Stickey\(^16\) from measurements by Weber, Fusu and Cassuto\(^17,18\) of the rate of reaction of \( \text{O}_2 \) with rhenium metal to form \( \text{ReO}_3 \) gas is included. The assumption necessary to obtain kinetic data by their method is equivalent to that used to calculate thermodynamic data from rates of vaporization determined by the Langmuir method\(^19\)—that complete equilibrium is maintained between the bulk solid and molecules adsorbed on the solid surface. The calculated value of the heat of formation of \( \text{ReO}_3 \) from the kinetic data is therefore a limiting value which (neglecting experimental error) cannot be more negative than the true heat of formation, but may be more positive by an amount that can only be determined by comparison with equilibrium data. The listed uncertainties from our measurements are those we would
usually assign from experience with the apparatus without consideration of uncertainties in partition functions. For the kinetic data, the uncertainty was estimated by Franklin and Stickney.

The third law calculations of Table V assign the value unity to the electronic partition function for ReO$_3$(g). This is a minimum estimated value. The actual electronic partition function may contribute the equivalent of several entropy units to the total partition function. An underestimate of the electronic partition function, for example, by the equivalent of three eu would make the calculated third law heats of formation of the present study too negative by about 3.6 kcal and the limiting value calculated from the kinetic measurements at much higher temperature too negative by about 7 kcal. In light of this uncertainty in value for the partition function, we place principal reliance on the two closely agreeing second law measurements of this study and recommend $-68 \pm 5$ kcal as a value for the heat of formation of ReO$_3$ gas at 298$^\circ$K. The quoted uncertainty indicates our 90% confidence limit.

The partition function assumed for Re$_2$O$_6$ gas may be low for the reason just discussed for ReO$_3$. On the other hand, the second law heat of formation for Re$_2$O$_6$ gas reported in Table V depends on corrections of observed intensities of the Re$_2$O$_6$ for the contribution presumed to arise from fragmentation of Re$_2$O$_7$. Uncertainties in both calculations are high, and a limiting value of $\Delta H_{298} \geq -212 \pm 20$ kcal is recommended.

The measurements of the oxygen partial pressure for the dissociation of solid dirhenium heptoxide to solid rhenium trioxide, Eq. (2), make possible a test of the internal consistency of reported values for the heats of formation of the two solid oxides (Table VI). The
estimated uncertainty in the oxygen pressure for the reaction is a factor of 2, which introduces only 0.3 kcal uncertainty into the calculated entropy of reaction, so that the heat of reaction 2 can be fixed by a third law calculation as 13.2 ± 2 kcal at 2090K. Selected values of -298.2 ± 2 kcal for the heat of formation of solid Re₂O₇ and -142.5 ± 2 kcal per mole of solid ReO₃ are consistent with this heat of reaction and agree reasonably well with most of the values of heats of formation that have been reported.

ACKNOWLEDGMENTS

This work was supported by the Metallurgy and Materials Branch of the U.S. Atomic Energy Commission. Comments by Alfred Buchler, Karl Gingerich, David J. Meschi, J. H. Norman, L. H. Rovner, and P. Winchell on a first draft of this paper were very helpful to us and are greatly appreciated.
REFERENCES

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Table I. Relative intensities of ions formed from the vapor from ReO$_7$(s) and from the Re+ZnO and Re+MgO reactions at 70 eV and their appearance potentials

<table>
<thead>
<tr>
<th>Ion</th>
<th>Intensity and Standard Deviation</th>
<th>Appearance Potentials (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>from ReO$_7$(s)</td>
<td>from Re+ZnO</td>
</tr>
<tr>
<td>ReO$_7^+$</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>ReO$_6^+$</td>
<td>91 ± 2</td>
<td>131 ± 12</td>
</tr>
<tr>
<td>ReO$_5^+$</td>
<td>17.4 ± 0.4</td>
<td>23 ± 2</td>
</tr>
<tr>
<td>ReO$_3^+$</td>
<td>276 ± 11</td>
<td>720 ± 260</td>
</tr>
<tr>
<td>ReO$_2^+$</td>
<td>154 ± 9</td>
<td>218 ± 52</td>
</tr>
<tr>
<td>ReO$^+$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

-18
Table II. $\Delta H^o_{298}$ calculated from weight loss data for the reaction $\text{Re}_2\text{O}_7(\text{s}) = 2\text{ReO}_3(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})$

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>$\Delta F^o_T$ (kcal)</th>
<th>Orifice area (cm$^2$)</th>
<th>$-\frac{\left(\Delta F^o_T - \Delta H^o_{298}\right)}{T}$</th>
<th>$\Delta H^o_{298}$ (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>430.9</td>
<td>7.38</td>
<td>0.01046</td>
<td>13.41</td>
<td>13.16</td>
</tr>
<tr>
<td>424.9</td>
<td>7.91</td>
<td>0.01046</td>
<td>13.42</td>
<td>13.61</td>
</tr>
<tr>
<td>424.6</td>
<td>7.60</td>
<td>0.034</td>
<td>13.42</td>
<td>13.30</td>
</tr>
<tr>
<td>423.7</td>
<td>7.16</td>
<td>0.001075</td>
<td>13.42</td>
<td>12.85</td>
</tr>
<tr>
<td>429.4</td>
<td>7.34</td>
<td>0.034</td>
<td>13.41</td>
<td>13.10</td>
</tr>
</tbody>
</table>
Table III. Weight loss data for ZnO-Re experiments

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°K)</td>
<td>1245</td>
<td>1177</td>
<td>1187</td>
</tr>
<tr>
<td>Time (sec)</td>
<td>$4.00 \times 10^4$</td>
<td>$1.60 \times 10^5$</td>
<td>$1.75 \times 10^5$</td>
</tr>
<tr>
<td>Weight loss</td>
<td>.0336</td>
<td>.0265</td>
<td>.0358</td>
</tr>
<tr>
<td>Clausing factor</td>
<td>.4</td>
<td>.4</td>
<td>.4</td>
</tr>
<tr>
<td>Area (cm²)</td>
<td>$6.42 \times 10^{-4}$</td>
<td>$6.42 \times 10^{-4}$</td>
<td>$6.42 \times 10^{-4}$</td>
</tr>
<tr>
<td>Corrected Partial Pressures (atm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) Zn(g)</td>
<td>$1.55 \times 10^{-4}$</td>
<td>$3.02 \times 10^{-5}$</td>
<td>$4.59 \times 10^{-5}$</td>
</tr>
<tr>
<td>(2) Re₂O₇(g)</td>
<td>$9.15 \times 10^{-6}$</td>
<td>$1.68 \times 10^{-6}$</td>
<td>$2.66 \times 10^{-6}$</td>
</tr>
<tr>
<td>(3) ReO₃(g)</td>
<td>$1.65 \times 10^{-6}$</td>
<td>$5.58 \times 10^{-7}$</td>
<td>$1.235 \times 10^{-6}$</td>
</tr>
<tr>
<td>(4) Re₂O₆(g)</td>
<td>$9.86 \times 10^{-8}$</td>
<td>$7.05 \times 10^{-8}$</td>
<td>$1.60 \times 10^{-7}$</td>
</tr>
<tr>
<td>Equilibrium Constants</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Re}_6 + 3\text{ZnO(s)} \rightarrow$</td>
<td>$6.2 \times 10^{-18}$</td>
<td>$1.5 \times 10^{-20}$</td>
<td>$1.2 \times 10^{-19}$</td>
</tr>
<tr>
<td>$\text{ReO}_3(g) + 3 \text{Zn(g)}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2\text{Re(s)} + 6 \text{ZnO(s)}$</td>
<td>$1.4 \times 10^{-30}$</td>
<td>$5.3 \times 10^{-35}$</td>
<td>$1.5 \times 10^{-33}$</td>
</tr>
<tr>
<td>$\text{Re}_2\text{O}_6(g) + 6 \text{Zn(g)}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2\text{Re(s)} + 7 \text{ZnO(s)}$</td>
<td>$2.0 \times 10^{-32}$</td>
<td>$3.8 \times 10^{-38}$</td>
<td>$1.1 \times 10^{-36}$</td>
</tr>
<tr>
<td>$\text{Re}_2\text{O}_6(g) + 7 \text{Zn(g)}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table IV. 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.

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>Experiment</th>
<th>1155</th>
<th>1145</th>
<th>1128</th>
<th>1189</th>
<th>1152</th>
<th>$\Delta H^0_{T}$ (2nd Law, kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re(s) + 3ZnO(s) $\rightarrow$ ReO$_3$(g) + 3Zn(g)</td>
<td>1 (13 points)</td>
<td>1155</td>
<td>263.7 $\pm$ 3.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 (11 points)</td>
<td>1145</td>
<td>266.7 $\pm$ 2.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 (13 points)</td>
<td>1128</td>
<td>264.7 $\pm$ 3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 (12 points)</td>
<td>1189</td>
<td>275.9 $\pm$ 2.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 (9 points)</td>
<td>1152</td>
<td>271.2 $\pm$ 2.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\Delta S^0_{Ave} = 137.8 \pm 3.0$ $\Delta H^0_{Ave} = 268.2 \pm 3.0$

2Re(s) + 6ZnO(g) $\rightarrow$ Re$_2$O$_6$(g) + 6Zn(g) | 1 (13 points) | 1155 | 452.0 $\pm$ 6.8 |
| | 2 (11 points) | 1145 | 458.0 $\pm$ 5.8 |
| | 3 (12 points) | 1128 | 453.5 $\pm$ 7.0 |
| | 4 (15 points) | 1175 | 465.3 $\pm$ 6.2 |

$\Delta S^0_{Ave} = 233.0 \pm 8.0$ $\Delta H^0_{Ave} = 457.9 \pm 6.0$

2Re(s) + 7ZnO(g) $\rightarrow$ Re$_2$O$_7$(g) + 7Zn(g) | 1 (13 points) | 1155 | 514.4 $\pm$ 8.3 |
| | 2 (11 points) | 1145 | 515.3 $\pm$ 4.6 |
| | 3 (13 points) | 1128 | 516.3 $\pm$ 5.9 |
| | 4 (15 points) | 1175 | 505.0 $\pm$ 6.3 |
| | 5 (10 points) | 1152 | 538.9 $\pm$ 9.3 |

$\Delta S^0_{Ave} = 267.8 \pm 7.8$ $\Delta H^0_{Ave} = 516.5 \pm 7.1$
Table V. Enthalpies of formation for ReO₃(g) and Re₂O₆(g) at 298°K

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Method of Calculation</th>
<th>ΔH°(298) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Norman et al.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZnO+Re</td>
</tr>
<tr>
<td>ReO₃(g)</td>
<td>Second law</td>
<td>-75.8, -90.6ᵃ</td>
</tr>
<tr>
<td></td>
<td>Third law</td>
<td>-62.7ᵃ</td>
</tr>
<tr>
<td>Re₂O₆(g)</td>
<td>Second law</td>
<td>-208.7 ± 20</td>
</tr>
<tr>
<td></td>
<td>Third law</td>
<td>-216.8 ± 4ᶜ</td>
</tr>
</tbody>
</table>

ᵃ Recalculated from the data of Norman, et al.⁵

ᵇ Calculated from Weber, et al.¹⁷,¹⁸ by the method of Franklin and Stickney.¹⁶

ᶜ This estimated uncertainty neglects the possible errors in estimated partition function. See text.
Table VI. Measured heats of formation of Re$_2$O$_7$(s) and ReO$_3$(s) and calculated heats of the reaction Re$_2$O$_7$(s) = 2ReO$_3$(s) + 1/2 O$_2$(g)

<table>
<thead>
<tr>
<th>Solid</th>
<th>$\Delta H_{P298}$ (kcal)</th>
<th>Heat of reaction (kcal)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReO$_3$</td>
<td>-83.0</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Re$_2$O$_7$</td>
<td>-297.5</td>
<td>131.5</td>
<td>20</td>
</tr>
<tr>
<td>ReO$_3$</td>
<td>-140.8 ± 0.9</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>Re$_2$O$_7$</td>
<td>-301.9 ± 1.8</td>
<td>20.3</td>
<td>21</td>
</tr>
<tr>
<td>ReO$_3$</td>
<td>-146.0 ± 3.0</td>
<td></td>
<td>22</td>
</tr>
<tr>
<td>Re$_2$O$_7$</td>
<td>-295.0 ± 2.0</td>
<td>2.8</td>
<td>22</td>
</tr>
<tr>
<td>ReO$_3$</td>
<td>-146.1 ± 0.8</td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>ReO$_3$</td>
<td>-140.7 ± 2</td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1. The $\text{Re}_2\text{O}_7(s) = \text{Re}_2\text{O}_7(g)$ reaction as a function of temperature and the dissociation pressure for the reaction $\text{Re}_2\text{O}_7(s) = 2\text{ReO}_3(s) + \frac{1}{2} \text{O}_2(g)$.

Fig. 2. The equilibrium constant for the reaction $\text{Re}(s) + 3\text{ZnO}(s) = \text{ReO}_3(g) + 3\text{Zn}(g)$ as a function of temperature.
Fig. 1.
Fig. 2.
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