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CONSTRUCTION OF A GLOVEBOX
THERMOGRAVIMETRIC ANALYSIS APPARATUS;
LANGMUIR AND KNUDSEN EXPERIMENTS
ON THE EVAPORATION OF Gd_2O_3
FROM 2140 TO 2600°K

by

Donald R. Messier

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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Metallurgy Division

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	4
INTRODUCTION.	4
APPARATUS.	6
EXPERIMENTAL PROCEDURES.	9
Crucibles	9
Temperature Calibration.	9
Gd ₂ O ₃ Evaporation	10
RESULTS	11
Langmuir Experiments	11
Knudsen Cell Experiments	13
Collected Data and Thermodynamic Calculations	16
DISCUSSION	18
ACKNOWLEDGMENTS	19
REFERENCES.	20

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Glovebox TGA Apparatus	6
2.	Electrical System of Glovebox TGA Apparatus.	7
3.	Water-cooling System for Furnace of Glovebox TGA Apparatus	8
4.	Vacuum-atmosphere System for Glovebox TGA Apparatus	9
5.	Cross Section of the Tungsten Knudsen Cell Used in Gd_2O_3 -evaporation Experiments.	9
6.	Typical Plots of Weight Loss vs Time for the Evaporation of a Gd_2O_3 Pellet in a Tungsten Crucible.	11
7.	Weight-gain Rates for the Knudsen Cell When Empty and When the Orifice is Closed.	13
8.	Pressure of $O(g)$ over $Gd_2O_3(s)$ Calculated from the Langmuir and Knudsen-cell Data.	17

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Langmuir-evaporation Results for a Gd_2O_3 Pellet Suspended from a Rhenium Wire	12
II.	Langmuir-evaporation Results for Gd_2O_3 Pellets Evaporated from a Tungsten Crucible	13
III.	Knudsen-cell Data for the Evaporation of Gd_2O_3	15

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ABSTRACT

An apparatus for high-temperature thermogravimetric analysis, consisting of a resistance furnace and recording microbalance, was constructed in a glovebox for eventual work with plutonium ceramics. The system was tested in vacuo for leaks, furnace control, and pyrometer calibration at furnace temperatures up to 2673°K.

Langmuir and Knudsen evaporation experiments were made with gadolinium sesquioxide in the temperature range from 2140 to 2600°K. Two sets of data obtained with the Knudsen cell yielded an average value of $\Delta H_0^\circ = 464.0 \pm 1.0$ kcal/mole for the assumed evaporation reaction

Enthalpy calculations based on the second and third laws of thermodynamics resulted in good agreement. The experimental results indicate that the evaporation coefficient may be much less than one.

INTRODUCTION

Interest in ceramic fast reactor fuels has focused attention on their high-temperature properties, but few data exist on the thermal stability of plutonium-bearing ceramics. The object of this program is, therefore, to obtain data on the thermal stabilities of plutonium compounds and mixed uranium-plutonium compounds that are of interest as fuel materials. This report covers the first phase of the program, namely, the construction and calibration of a high-temperature thermogravimetric analysis (TGA) apparatus for use in a glovebox.

More knowledge of evaporation kinetics can be gained with the TGA apparatus, which includes a recording microbalance, than is obtainable

by the conventional periodic weighing technique. For example, a continuous record of weight loss enables identification of outgassing effects. Also, it eliminates uncertainty associated with the time required to reach temperature. A further advantage is reliable detection of congruent evaporation. Finally, continuous weighing enables runs to be made conveniently at several temperatures without removal of a specimen from the system.

In order to discover potential difficulties before closure of the glove-box, the apparatus and operating procedures were thoroughly tested through experimentation with a nonfissile material, gadolinium oxide. This particular oxide was chosen because:

1. It may have value as a stabilizing agent in (U,Pu)O₂ fuels.
2. The temperature range, 2150 to 2600°K, wherein its vapor pressure is significant, is similar to that of experiments planned for (U,Pu)O₂.
3. Experimental data are available for comparison with the results.¹

Experimental data were desirable, both for calibration of the apparatus, and if the two independent measurements agreed, to establish confidence in the vapor-pressure data.

Two techniques were chosen for the evaporation experiments:² the Langmuir technique, which measures the rate of evaporation from an exposed surface, and the Knudsen-cell technique, which measures the rate of effusion of vapor from a small orifice in a cell containing material assumed to be in equilibrium with its vapor. Because of the large exposed surface area of the specimen, the Langmuir technique yields larger rates at a given temperature than those measured by the Knudsen technique. The use of both techniques therefore allows measurements to be made over a greater temperature range than is possible by using either technique alone.

Additional information of both theoretical and practical interest can be obtained by comparing the rates per unit area measured by both techniques. The Knudsen measurement gives the maximum possible rate. The Langmuir, or free evaporation, rate sometimes is much less than the Knudsen rate. Such behavior indicates a slow step in the evaporation process, and the system is then said to have a low evaporation coefficient. Since low evaporation coefficients have been observed in other oxide systems,³ it was of interest to determine if Gd₂O₃ behaved similarly.

APPARATUS

The portion of the apparatus located in the glovebox was photographed (see Fig. 1) before the glovebox windows were installed. The vacuum system and most of the water-cooling system are located underneath the glovebox.

106-8915

Fig. 1. Glovebox TGA Apparatus

The automatic-recording, semimicro balance* (upper part of Fig. 1) has a 100-g capacity. A trace on a recorder chart can be read to ± 0.01 mg, and is reproducible to ± 0.03 mg. For the greater safety requisite in glovebox work, the Pyrex bell jar supplied with the balance was replaced with one of stainless steel. Sandwiches of lead brick and cork sheet, which rest on an aluminum-alloy plate, support the balance. The plate itself rests on sponge-rubber pads attached to brackets on the glovebox frame. The balance is connected to the furnace and pumping port with stainless steel

* Wm. Ainsworth and Sons, Type 14.

bellows. These steps were taken to minimize vibration, which might have been a problem. Thus far, vibration effects have been minor and have not seriously affected the system performance.

The specimen in the balance is suspended from the weighing pan into the furnace on a chain made from W-26w/oRe wire, 0.025 cm in diameter. This wire is more ductile than pure tungsten wire, and can be bent and twisted with little trouble.

Tungsten-mesh or tantalum heating elements and tungsten or tantalum heat shields can be used interchangeably in the furnace.* The heating elements are 5.1 cm in diameter and 10.2 cm long. With the tungsten element and heat shields, the furnace can be operated in vacuo, or in inert or reducing atmospheres. With a power input of 13 KVA, the furnace operates to about 2673°K in vacuum and 2573°K in helium.

A schematic of the electrical system of the apparatus appears in Fig. 2. Furnace temperature control is achieved by a power-control system

106-8908

Fig. 2. Electrical System of Glovebox TGA Apparatus

*Marshall Products Company Model 900.

incorporating a thermal converter,* a null detector,** and a CAT control unit.† The set point either is positioned by hand with a set-point unit,†† or is controlled automatically with a Data-Trak programmer.‡ A 15-KVA silicon-controlled rectifier†† supplies the power. As shown in Fig. 2, electrical interlocks protect the system against failures both of vacuum and of flow of cooling water. This system successfully controls from zero to full power.

A schematic of the water cooling system appears in Fig. 3. Cooling-water flow in the recirculating contaminated-coolant system is supplied by a pump‡‡ capable of delivering 38 liters (10 gal) per minute at a pressure of 3.52 kg/sq cm (50 psi). The furnace-cooling system has six separate circuits, each protected by a flow switch to guard against the possibility of blockage of one circuit without a change in the overall flow rate.

106-8914

Fig. 3. Water-cooling System for Furnace of Glovebox TGA Apparatus

* Lincoln No. 10781-1, Leeds and Northrup Company.

** Leeds and Northrup Company No. 9834-2.

† Leeds and Northrup Company.

†† Barber-Colman Company.

‡ Research, Incorporated.

‡‡ Fostoria Corporation.

106-8911

Fig. 4. Vacuum-atmosphere System for Glovebox TGA Apparatus

and temperature-calibrations runs were made with use of an open crucible that was 1.59 cm in OD and 1.59 cm high.

A cross section of the tungsten Knudsen cell used for the equilibrium evaporation measurements is shown in Fig. 5. The harness for the cell was made from 0.076-cm-diameter W-26w/oRe wire. The hole in the bottom lid was 0.063 cm in diameter, and was used as a usual target in measuring temperature. The ratio of the cavity diameter to the hole radius was 30, nearly ideal for approximating blackbody conditions.⁴ Two different top lids were used: one had a 0.0889-cm-diameter hole and the other a 0.169-cm-diameter hole. The lengths and diameters of the holes were measured with a micrometer and with pin gauges, respectively. Microscopic observation showed the holes to be round and untapered.

Temperature Calibration

Temperature is measured with a Micro-Optical pyrometer.* The optical path traverses a right-angle prism, a

*Pyrometer Instrument Company.

The arrangement of the vacuum and atmosphere-control system is shown in Fig. 4. The filters are provided to keep the system as free from contamination as possible.

EXPERIMENTAL PROCEDURES

The procedures for testing the apparatus involved calibration of the systems for measurement of weight and temperature, and evaporation measurements with Gd_2O_3 .

Crucibles

All of the crucibles that were used were made from tungsten. Some of the Langmuir evaporation runs

106-8909

Fig. 5. Cross Section of the Tungsten Knudsen Cell Used in Gd_2O_3 -evaporation Experiments

quartz window in the glovebox baseplate, and a quartz window in the bottom of the furnace. The window-prism system and pyrometer were calibrated with a standard lamp located in a blackbody enclosure and certified by the National Bureau of Standards. The correction was substantial, amounting to 100°K at an object temperature of 2600°K. Next, melting points of several metals were measured under actual operating conditions in order to verify blackbody conditions, to detect possible temperature gradients in the crucibles, and to confirm the standard-lamp results with absolute standards.

The melting points of rhodium, nickel, platinum, and iron were determined by heating specimens in vacuum on tungsten setter plates in the open tungsten crucible and observing the temperature at which there was visual evidence of melting. Nickel gave a correction 31°K less than that for the standard lamp. The corrections for iron and platinum were -5 and -15°K, respectively. All metals except iron obviously reacted with tungsten. Rhodium reacted to such a degree as to make a measurement impossible. Platinum that had been heated several times on the same tungsten setter had a melting point 20°K higher than that of platinum heated only once. The observed elevation of the melting point accords with the dissolution of tungsten in platinum indicated by the tungsten-platinum phase diagram.⁵ Since reaction with tungsten was unavoidable, thoria grain was tried as a setter material. The melting point of platinum on thoria, measured with the specimen in the Knudsen cell, gave a correction 3°K greater than that indicated by the standard lamp. Rhodium again appeared to react.

The calibration also was made by comparing pyrometer and thermocouple measurements to 1773°K. These were in excellent agreement.

The value found for the melting point of platinum and thermocouple calibration both show that the standard-lamp calibration was reliable. A correction curve calculated from the lamp-calibration points was used to correct the temperature measurements obtained during experiments.

The temperature reported for each run was the corrected average of eight or more determinations by two observers.

Gd₂O₃ Evaporation

The material tested in the evaporation experiments was 99.9% pure Gd₂O₃,* which was received in the form of a fine, hygroscopic powder. X-ray patterns of this material showed only lines corresponding to the cubic "C" form of Gd₂O₃.⁶

The powder was pressed into pellets without binder, and the pellets were sintered in vacuum for one hour at 2123°K. Only two pellets, designated G-1 and G-4, were used for the entire series of evaporation experiments. Pellet G-4 had an axial hole for suspension during free-evaporation

*American Potash and Chemical Corporation.

experiments. The dimensions of the sintered pellets were measured with a micrometer. G-1 was 5.820 mm in diameter and 4.450 mm thick; G-4 was 11.00 mm in diameter and 2.39 mm thick. The areas used in the calculations of Langmuir evaporation rates were determined from micrometer measurements.

Langmuir-evaporation experiments were done with pellets G-1 and G-4 in an open tungsten crucible, and with pellet G-4 suspended on a rhenium wire. Pellet G-4 was then broken into several pieces for loading into the Knudsen cell, for tests made both with the hole open and with the hole closed. The hole was closed by fitting a disc of 0.0025-cm tungsten foil into the depression in the cell lid.

The tungsten crucible and cell were thoroughly outgassed before each series of runs. An evaporation run was started by heating the specimen to the desired temperature at $50^\circ\text{K}/\text{min}$. This rate was slow enough to insure outgassing of a specimen on all heatings except the initial one. Weight-loss rates were measured at several temperatures without breaking vacuum or removing the specimen. A pressure of only 1 to 3×10^{-6} Torr obtained during the runs. At the conclusion of a series of runs, the specimen was cooled no faster than $50^\circ\text{K}/\text{min}$ so as to avoid fracture by thermal shock.

In the Langmuir experiments, weight-loss rates were high enough to change the dimensions of the pellets. Pellet G-1 was so shaped as to change appreciably in dimensions. Periodic measurements of dimension made possible the calculation of specimen area as a function of weight loss. A graph of area vs weight loss was used to determine the average pellet area for a run at a particular temperature.

43790

Fig. 6. Typical Plots of Weight Loss vs Time for the Evaporation of a Gd_2O_3 Pellet in a Tungsten Crucible

RESULTS

Langmuir Experiments

A series of plots of weight loss vs time for pellet G-1 are shown in Fig. 6. Similar, linear evaporation rates were observed in all of the Langmuir runs.

Evaporation runs in the tungsten crucible caused both pellets to change from white to black; but pellet G-4 subsequently changed from black to light gray on vacuum heat treatment at 2213°K while suspended from a rhenium wire. The latter color change was apparently due to loss of tungsten contamination.

The effect of the contamination by tungsten on the weight-loss rates was checked by comparing the weight change of a specimen with that of the tungsten setter plate. In a series of runs from 2150 to 2380°K, pellet G-1 lost a total of 98.5 mg, while the setter plate lost only 0.6 mg, indicating that the reaction effect was minor in this temperature range.

X-ray patterns obtained after evaporation tests showed that the structure of the gadolinia had changed from the cubic "C" type to the monoclinic "B" type. This phase transformation is well-known.⁶

The results of the evaporation experiments in which pellet G-4 was suspended on a rhenium wire are given in Table I. The temperatures given in Table I were obtained by subsequently sighting on the empty tungsten crucible at the same furnace set points as were used for the specimen. The blackbody conditions were such that sighting on the specimen would have given inaccurate results.

TABLE I. Langmuir-evaporation Results for a Gd_2O_3
Pellet Suspended from a Rhenium Wire

Temp, °K	S, cm ²	Weight Loss Rate x 10 ⁵ , g sec ⁻¹
2155	2.89	0.167
2213	2.71	0.395
2273	2.69	1.07
2323	2.66	2.75
2213	2.64	0.425
2153	2.58	0.245
2213	2.57	0.541
2273	2.56	1.42
2163	2.55	0.258
2333	2.54	3.56
2273	2.53	1.42
2213	2.52	0.566

Data obtained from evaporation runs on pellets G-1 and G-4 in the open tungsten crucible are given in Table II. The quantities " ℓ " and " a " are, respectively, the inside depth and radius of the crucible; " W " is the Clausing correction factor, obtained from Dushman.² The surface areas of the specimens, " S ," were calculated on the assumption that only the top and sides of the pellet contributed to the evaporating surface area.

TABLE II. Langmuir-evaporation Results for Gd_2O_3 Pellets
Evaporated from a Tungsten Crucible

$l = 14.5 \text{ mm}$; $a = 8.15 \text{ mm}$; $W = 0.538$

Temp, °K	S, cm^2	Weight Loss Rate $\times 10^5$, g sec^{-1}	Temp, °K	S, cm^2	Weight Loss Rate $\times 10^5$, g sec^{-1}
2260	1.08	2.32	2265	0.889	1.94
2156	0.970	0.304	2151	1.72	0.364
2211	0.966	0.909	2196	1.72	0.975
2274	0.959	2.34	2264	1.71	2.66
2337	0.948	6.27	2320	1.70	6.95
2149	0.941	0.333	2361	1.70	13.6
2380	0.933	12.6	2264	1.69	2.75
2380	0.913	11.5	2191	1.69	1.02
2324	0.898	5.05	2144	1.69	0.447

106-8912

Fig. 7: Weight-gain Rates for the Knudsen Cell When
Empty and When the Orifice is Closed

Knudsen Cell Experiments

The Knudsen cell runs were made at temperatures up to 2600°K . Since the vapor pressure of tungsten becomes appreciable at the higher temperatures, the need for correcting the measured rates for the weight loss of the cell was anticipated. Runs, therefore, were made with the empty cell and with the loaded cell with the hole closed. Surprisingly, the correction was for a constant weight gain. The results of the empty and closed cell runs are shown in Fig. 7.

The possibility that the weight gain was caused by the deposition of material on the suspension wire or balance pan was ruled out because the weight of the suspension system remained constant. That the crucible actually did gain weight was confirmed by independent measurements on an analytical balance.

The most plausible explanation for the weight gain is vapor transport of tungsten from the heating element to the crucible. If it is assumed that the partial pressure of tungsten in

the system is that of tungsten at the temperature of the heating element; the expression for the crucible weight gain rate is

$$R_o = R_d - R_e,$$

where R_o is the observed weight-gain rate, R_d is the rate of tungsten deposition from the element at temperature T_d , and R_e is the rate of tungsten evaporation from the crucible at temperature T_e .

In order to calculate a weight-gain rate to compare with the observed rate, the temperatures of the cell and element were determined for numerous settings of furnace power. A plot of temperature vs set point showed a difference of about 60 to 70°K between temperatures of element and cell in the range from 2373 to 2673°K. The observed temperatures, combined with data for tungsten vapor pressure, were used to calculate theoretical rates of weight gain for the crucible.² The calculated rate curve, shown as a dashed line in Fig. 7, agrees quite well with rates for the empty cell. The scatter in the data points is mainly due to the smallness of the measured weight changes (about one mg), causing minor deviations to result in relatively large percentage deviations from the most probable values.

The solid line in Fig. 7 is drawn through the data points for the closed-cell values, and this plot was used to correct the evaporation data. Although a slight amount of cell leakage, if it existed, may have caused some of these rates to be too low, the lower values may be due only to the considerable scatter in the lower-temperature data.

Because of the scatter, the effect of possible errors in the correction on the final evaporation rates should be considered. It is believed that the effect is small for two reasons: (1) the greatest uncertainty in the correction is at the lower temperatures where its magnitude is least, and (2) the percentage correction is small, ca. 5%, particularly for the runs with the larger cell orifice. For runs with the smaller cell orifice, the percentage correction amounted to about 30% of the total rate. This correction of higher percentage can, as already pointed out, be expected to result from application of the same absolute correction to both high and low total rates at equivalent temperatures.

As in the Langmuir experiments, the Knudsen-cell weight-loss rates were linear, but nonlinear rates sometimes obtained for the first few hours of heating after the specimen had been exposed to the room atmosphere. The nonlinearity was attributed to outgassing.

The Knudsen-cell evaporation data are given in chronological order in Table III. The symbol " ℓ " refers to the hole length and " a " to the hole radius. The dimensions given are corrected to 2500°K by use of a tungsten expansion coefficient of 5.6×10^{-6} per °K.⁷

TABLE III. Knudsen-cell Data for the Evaporation of Gd_2O_3

Temp, °K	Weight Loss Rate $\times 10^7$, g sec ⁻¹	$P_{\text{GdO}} \times 10^5$, atm	$P_{\text{O}} \times 10^6$, atm	$\Delta H_{\text{O}}^\circ$, kcal
Cell No. 1: $\ell = 1.832$ mm; $a = 0.450$ mm; $W = 0.356$				
2572	4.99	1.84	2.80	463.6
2443	1.32	0.474	0.723	460.8
2538	3.41	1.25	1.90	463.3
2505	2.63	0.956	1.45	461.8
2470	1.48	0.535	0.813	463.8
2567	4.82	1.78	2.70	463.2
2592	6.40	2.37	3.59	462.9
2413	0.753	0.269	0.408	463.5
Cell No. 2: $\ell = 1.760$ mm; $a = 0.855$ mm; $W = 0.507$				
2505	10.4	0.733	1.11	465.7
2472	7.63	0.532	0.807	464.1
2453	5.62	0.392	0.597	465.2
2524	14.2	1.00	1.52	464.6
2415	3.78	0.261	0.398	464.3
2384	2.51	0.172	0.261	464.0
2353	1.64	0.112	0.169	464.5
2532	14.4	1.02	1.55	465.5
2557	19.4	1.38	2.10	465.2
2572	22.5	1.61	2.44	465.6

Average $\Delta H_{\text{O}}^\circ = 464.0 \pm 1.0$ kcal.

Although some Gd_2O_3 was deposited on the cell lid, trends are absent in the data. Furthermore, no deposition within the orifices of the cells could be observed with a microscope.

After the completion of the evaporation runs, specimen G-4 was checked for possible changes in stoichiometry. The specimen was reoxidized by heating to constant weight in oxygen at 1473°K for 3 hr. Restoration of the original white color was evidence of reoxidation. On the basis that the oxygen-to-metal ratio in the oxidized specimen was 1.50, the ratio in the evaporated specimen was 1.49.

A final cell experiment determined the extent of reaction with tungsten. Complete evaporation of an 88.4 mg chip of Gd_2O_3 from cell No. 2 at 2570°K caused the cell to lose only 0.8 mg. The amount of reaction, therefore, was small even at a temperature near the maximum attained in a run. The weight loss given is corrected, as usual, for the tungsten deposition.

Collected Data and Thermodynamic Calculations

Panish's mass-spectrometer data indicate that the ratio of gadolinium metal to GdO gas in the vapor above Gd_2O_3 is immeasurably small in the temperature range from 2000 to 2500°K.⁸ Calculations by White *et al.* confirm this conclusion.¹ In the thermodynamic calculations, therefore, the following reaction is assumed:

Partial pressures of oxygen and GdO gases were calculated for the out-of-crucible Langmuir data from the expression

$$P_K (\text{atmos}) = \frac{2.26 \times 10^{-2} m_i}{S} \left(\frac{T}{M_i} \right)^{1/2},$$

where m_i is the weight-loss rate (g sec^{-1}) for a given vapor species, S is the specimen surface area, T is the absolute temperature (°K), and M_i is the molecular weight (g mole^{-1}). The expression used for the Knudsen cell and crucible data is

$$P_K (\text{atmos}) = \frac{2.26 \times 10^{-2} m_i}{Wh} \left(\frac{T}{M_i} \right)^{1/2},$$

where W is the Clausing correction factor, and h is the cell-orifice area or crucible-bore area. For the Knudsen-cell and out-of-crucible Langmuir calculations, it was assumed that P_K was equal to the equilibrium pressure for each vapor species. Assuming that the analysis given by Rossman and Yarwood⁹ applies, equilibrium pressures were calculated from the crucible data with use of the expression

$$P_{\text{eq}} = P_K \left(1 + \frac{Wh}{\alpha S} \right),$$

where α is the evaporation coefficient. Alpha was assumed to be equal to one. Figure 8 is a semilog plot of oxygen pressure vs $1/T$ for all of the experimental data. Equations that fit the data are

$$\log_{10} P_{\text{O}} = 8.316 \pm 0.363 - \frac{(35.342 \pm 0.814) \times 10^3}{T} \quad (\text{Langmuir});$$

$$\log_{10} P_{\text{O}} = 6.813 \pm 0.486 - \frac{(31.774 \pm 1.219) \times 10^3}{T} \quad (\text{Cell No. 1});$$

$$\log_{10} P_{\text{O}} = 6.830 \pm 0.160 - \frac{(31.977 \pm 0.396) \times 10^3}{T} \quad (\text{Cell No. 2}),$$

45533

Fig. 8. Pressure of O(g) over Gd₂O₃(s) Calculated from the Langmuir and Knudsen-cell Data

are 436.6 ± 16.6 and 438.8 ± 5.3 kcal/mole for cells No. 1 and 2, respectively. Third-law heat values, for the average temperature for each series, were calculated with use of the entropy data of White *et al.*¹ These are 437 and 439 kcal/mole for cells No. 1 and 2, respectively. Confidence in the measurement procedure is justified by the good agreement of all of the values.

A dissociation energy for GdO(g) was calculated from $D_O^\circ(\text{GdO}) = -\frac{1}{2} \Delta H_O^\circ(\text{vaporization reaction}) - \frac{1}{2} \Delta H_O^\circ(\text{Gd}_2\text{O}_3 \text{ formation}) + \Delta H_O^\circ(\text{gadolinium vaporization}) + \frac{3}{4} D_O^\circ(\text{O}_2 \text{ dissociation})$. $\Delta H_O^\circ(\text{Gd}_2\text{O}_3 \text{ formation})$ was obtained from White *et al.*,¹ $\Delta H_O^\circ(\text{Gd vaporization})$ from Habermann and Daane,¹¹ and $D_O^\circ(\text{O}_2 \text{ dissociation})$ from the JANAF tables.¹⁰ A value of $D_O^\circ(\text{GdO}) = 7.37$ eV was calculated for the dissociation reaction

Unfortunately, this has not been checked by any other method.

where P_O is the oxygen pressure (atmos) and T is the absolute temperature (°K). Because the Langmuir data were not internally consistent, they were not used in the following thermodynamic calculations.

The third-law heat values given in Table III are for the assumed vaporization reaction at 0°K. They were calculated with use of the free energy functions for Gd₂O₃(s) and GdO(g) given by White *et al.*¹ Free energy functions for O(g) were obtained from the JANAF tables.¹⁰ The error given for the average ΔH_O° value of 464.0 ± 1.0 kcal/mole is the average deviation.

Second-law heats for the vaporization reaction were obtained from least-squares slopes of plots of $\log K$ vs $1/T$ for the two sets of cell data. The values

DISCUSSION

The linear evaporation kinetics observed in all of the experimental runs indicate that Gd_2O_3 evaporates congruently between 2140 and 2600°K.

The results indicate that the modified Langmuir technique, whereby evaporation runs are made on pellets in open crucibles, can yield data equivalent to those obtained in free evaporation experiments. The good agreement between the rate of evaporation of pellet G-4 in the crucible with that for the pellet out of the crucible indicates that correct assumptions were made in obtaining vapor pressures from the crucible data. Also, the vapor pressures calculated from the two sets of crucible data agreed despite geometrical differences between the two pellets. The assumption that the portion of the pellet resting on the plate does not contribute to the area of the evaporating surface therefore appears good. Furthermore, the dimensional changes in pellet G-1 due to evaporation are in accord with this assumption. Since the decrease in pellet height was only half the decrease in diameter, evidently only the top and sides had been evaporating.

Pellet G-4, evaporated from both the tungsten crucible and rhenium wire, apparently changed from white to black mainly because of tungsten contamination. The final light gray color, observed on tungsten-free surfaces, is due to preferential loss of oxygen.

Although the Knudsen cell results indicate that the evaporation coefficient α may be less than one, the following discussion points out why an accurate calculation of α was impossible.

Rosenblatt¹² has shown that the effective evaporating surface area of a porous specimen may be much greater than its geometric area, particularly when the evaporation coefficient is less than one. Experimental measurements yield only the product αS , where S is the evaporating surface area. It is therefore evident that the value obtained for α depends upon the value assumed for S .

Through the assumption that the evaporating surface area was equal to the cell bore area (i.e., that the specimen completely covered the bottom of the cell), α was calculated to be 0.077 from the two sets of Knudsen cell data. If this low value of α had been used in calculating the Langmuir data, the Langmuir vapor pressures shown in Fig. 8 would be higher by an order of magnitude. On the other hand, the surface areas used in calculating the Langmuir data were undoubtedly smaller than the true evaporating surface areas.¹² Because these two effects tend to cancel each other, considerable uncertainty exists concerning the absolute magnitudes of the Langmuir vapor pressures. The good agreement between the Langmuir and Knudsen vapor pressures in the region of overlap thus appears fortuitous, and it does not rule out the possibility of a low evaporation coefficient.

Despite the uncertainties in the absolute magnitudes of the Langmuir data points, the fact that the slope of the Langmuir plot is steeper than those of the Knudsen plots also suggests a low evaporation coefficient. The evidence that α is less than one is consistent with the results of other oxide investigations.³ However, additional experimental work would be necessary to definitely confirm this result.

It is possible that the weight losses due to the tungsten reaction and oxygen-loss occur at the very beginning of a run before congruent evaporation obtains. Even if this is not the case, it can be shown that these effects are so small as to have a negligible effect on the thermodynamic calculations. By use of the tungsten oxide data of DeMaria *et al.*,¹³ one can calculate that the most probable reaction is

The experimental results indicate that x is about 0.01 and that y is 0.02. If one calculates free energies by adding

to the above reaction, the results are identical, within experimental error, to those given. In addition, because one is deriving an integral value for the free energy of the vaporization reaction, the small deviation from stoichiometry has no effect on the results.

The $\Delta H^\circ_{\text{O}}$ value of 464.0 ± 1.0 kcal/mole obtained from this study is higher than the previously reported value of 453.3 kcal/mole.¹ Ames' recently reported value¹⁴ of 461.7 kcal/mole is, however, in excellent agreement with the present results.

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