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VAPOR-SOLID EQUILIBRIA IN THE URANIUM OXIDE-OXYGEN SYSTEM

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Carl Albert Alexander, B.S., M.S.

********

The Ohio State University
1961

Approved by

[Signature]

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INTRODUCTION

Uranium oxides are of interest not only because of their practical application as fuel for power reactors, but also because of the complex nature of the uranium oxide-oxygen system. This system is of theoretical interest since there are variable oxidation states prevalent in the system, and it also is an excellent example of a non-stoichiometric binary system.

It is doubtful whether any oxide other than water has been as thoroughly investigated as the uranium oxides, but most of the experimental programs have been conducted at relatively low temperatures. On the other hand, possible applications of the oxides may involve much higher temperatures. Metallic and composite fuel elements seem to be capable of operation at temperatures of several hundred degrees centigrade. It would seem that one of the most obvious applications for a ceramic fueled reactor would be a small power reactor which could gain high efficiency by operation at temperatures over a thousand degrees centigrade.

As far as resistance to melting is concerned, it should be possible to operate an all ceramic reactor well above this temperature; however, other considerations such as solid-solid reactions, disproportionation, vapor phase transport, and possible fuel-coolant reactions would undoubtedly become serious factors before melting temperatures of refractory oxides are encountered. In order to predict such reactions so that a feasible design may be realized, it is necessary to have
reliable thermochemical data. In fact, the availability of such data for uranium oxides would be a common requirement for all reactor concepts, regardless of the moderator, fuel element design, or coolant employed.

Aside from these purely practical reasons for obtaining thermochemical data, vapor-solid equilibria for oxide systems seem to be a research area that has not been investigated. The techniques employed in the present investigation are not limited to uranium oxides or to oxides in general, but afford a means by which much information concerning the high temperature stability of many systems may be investigated. The minimum amount of information to be gained from such a study is the vapor density of the volatile products, while the maximum would be a complete thermodynamic description of the system. The position between these two extremes is strongly dependent on the nature of the system under investigation and whether additional information may be incorporated to extend the usefulness of the data. With uranium oxide, nearly a full description of the system is possible.

The purpose of this investigation then, is to define the uranium oxide-oxygen system at elevated temperatures. The approach is by means of vapor-solid experimental determinations used in conjunction with other pertinent information about the system in an effort to derive a set of consistent thermodynamic functions and a phase diagram which indicates the pressure-temperature-composition relationships in the uranium oxide-oxygen system.
LITERATURE

The literature contains literally hundreds of references to uranium oxides and their properties. An exhaustive survey of all the literature, including much project literature which would otherwise not be available, has been made by Katz and Rabinowitch\(^1\). This survey covers the period to 1950. An annotated bibliography containing over three hundred references concerning uranium oxides has been completed by the Bureau of Standards\(^2\), and a book has just been published under the auspices of the Atomic Energy Commission\(^3\) containing over seven hundred pages devoted to the properties of \(\text{UO}_2\).

With one exception, none of the published data appearing prior to 1950 is pertinent to this investigation; however, from an historical standpoint some of the early literature is of interest.

Investigations in the Eighteenth and Nineteenth Century

The first published report involving uranium oxides was that of Klaproth\(^4\), the discoverer of uranium. While working with pitchblende he reduced this form of \(\text{U}_3\text{O}_8\) with carbon, and due to the lustrous black appearance of the reaction product, he considered that he had produced a metal.

That uranium metal could not be produced in this manner was demonstrated by Peligot\(^5\) in 1842 who concluded that Klaproth had produced uranium dioxide. Reducing agents other than carbon were employed by
Herman who obtained the dioxide from the higher oxides by ignition with sulphur and ammonium chloride. During this time period there was little attempt to obtain thermochemical data, although in 1840 Regnault obtained specific heat values for uranium dioxide at the boiling point of water which are in good agreement with currently accepted values.

The Twentieth Century to 1940

The color changes occurring in uranium trioxide under various conditions of heat treatment was investigated by both Huttig and von Schroeder, and Jolibcis and Bossuet studied the decomposition of UO3 in vacuum at moderate temperatures.

The work of Biltz and co-workers, especially that of Biltz and Muller, was the first serious step to define the uranium oxide-oxygen system. By use of a tensimetric apparatus consisting of a furnace, quartz reaction tube, gas burette, and manometer, they were able to determine the oxygen dissociation pressure as a function of temperature.

In addition to determining the pressure, their use of a known system volume in conjunction with the gas burette allowed them to determine the amount of oxygen in the sample at temperature, hence, they were able to simultaneously determine the dissociation pressure and the O/U ratio of the condensed phase. They investigated the composition region from an O/U ratio of 3.00 down to about 2.2 and to a temperature of over 1400 K. They found at a fixed temperature, a region where the dissociation pressure changed rapidly with temperature extending from an O/U ratio of 3.00 down to about 2.6. This was followed by a region where the dissociation pressure was constant with changing composition. This
persisted to an O/U ratio of between 2.2 and 2.3. Below this composition the dissociation pressure again decreased rapidly with composition. They were not able to define the system at O/U ratios below 2.2 because of the low values of the dissociation pressure at temperatures attainable with their quartz apparatus. On the basis of the phase rule, they interpreted their results to indicate that a monophasic region existed from a composition of UO$_3$ to UO$_{2.61}$. At compositions below UO$_{2.61}$ and above about UO$_{2.3}$, a two-phase region existed. Below a composition of UO$_{2.3}$ a monophasic region again was found. One notable feature of their work was that U$_3$O$_8$ (UO$_{2.67}$) was not a distinct phase but only a particular composition in a monophasic region.

Another experiment carried out in Germany during this period was unrelated to investigations of the uranium-oxygen system, but had a profound effect on the direction of research for years to come. Hahn and Strassmann in 1939 discovered that fission of the uranium nucleus was possible with low energy neutrons. When news of this reached the United States, the basis for the Manhattan Project was established.

Research on the Manhattan Project and During the Post-War Years

Extensive research was conducted during this period at the national laboratories and at selected universities and research institutes throughout the country. Much of the data was initially classified and even on declassification, has not appeared in the open literature. Katz and Rabinowitch$^1$, in their book, The Chemistry of Uranium, have reviewed this project literature as well as reports in
the published literature prior to 1950. It is from this source that the following account of research during and immediately after the war has been obtained.

It is somewhat surprising that there was no attempt to duplicate or expand on Biltz and Muller's work during this period since two groups were active in determining the fundamental thermodynamic properties of uranium oxides; Brewer at Berkeley, and MacWood and Altman at University of California Radiation Laboratory.

Most of the experimental work on the uranium-oxide system was performed by X-ray diffraction investigations performed on quenched samples, a technique that had proved successful on silicate systems. Biltz and Muller had reported that transitions occurring in the uranium-oxygen system were "rapid and reversible"; however, much of the literature of the time was based on data taken from samples cooled to room temperature.

One of the most startling discoveries of the period made by diffraction study, was Zachariasen's finding at the University of Chicago of an oxide with a lower O/U ratio than 2.00. The O/U ratio was found to be 1.75. A possible analogy to Th$_4$S$_7$ was cited by Zachariasen. This discovery meant that either the UO$_2$ phase extended below an O/U ratio of 2.00 or that a new phase was present. Work at Battelle during this period, consisting of long-time annealing experiments with UO$_2$ and metallic uranium in contact, failed to substantiate this finding. UO was found to be the only sub-oxide in the uranium-uranium dioxide portion of the uranium-oxygen system.
Another case where the diffraction results differed markedly from previous results was a report by the Ames group that an oxide single phase of the composition U$_2$O$_5$ existed. This was in complete disagreement with the results of Biltz and Muller and, if true, would indicate that their tensimetric data were in serious error.

Perhaps the best summary of the status of the uranium oxide-oxygen system was that prepared by Brewer, who considered the more recent work plus the work of Biltz and Muller. From the various data he calculated volatilities of higher oxides (based on a weight loss reported by Biltz and Muller), free energies of formation, and, in general, commented upon the regions where the various investigators agreed and disagreed. Prior to 1955, this review by Brewer could be considered the outstanding contribution leading to understanding of the system for the whole war time and post-war period.

From 1955 to Present

Significant contributions have been made, starting in 1955, with the high temperature diffraction investigation of Gronvald. In his investigation, mixtures of UO$_2$ and U$_3$O$_8$ were put in sealed capsules and annealed for extended periods and then X-ray powder patterns were made at temperatures below 1000 C. The general features of his investigation were that there are three phases of uranium oxide (at least) as UO$_2$, U$_4$O$_9$, and U$_3$O$_8$. There is some evidence that a tetragonal U$_3$O$_7$ phase may exist at lower temperatures (a few hundred degrees) but it has not been demonstrated at this time whether this is a thermodynamically stable
phase or an intermediate structure during low temperature oxidation of uranium oxides. Gronvold found that the solubility of oxygen in UO₂ goes from essentially zero at temperatures from 25 to 200 °C, to O/U ratios of 2.2 at temperatures of 600 to 700 °C.

At the U₃O₈ end of the system he found the phase boundary to be at 2.60 at over 500 degrees, with the boundary shifting to lower O/U ratios at higher temperatures, reaching 2.56 at around 700 °C. This observation was the only one in serious disagreement with Biltz and Muller, who found the phase boundary to be above 2.60 at temperature of 1160 °C. Although it is possible there is a solubility reversal at elevated temperatures, so that both sets of data are correct, this is considered to be highly unlikely. Hoekstra and Siegel have performed extensive X-ray analysis of the system and concluded that the boundary occurs at 2.56.

An investigation of dissociation pressures over the various phases of uranium oxide was made by Blackburn. He investigated the phases at pressures lower than was possible by Biltz and Muller by use of an effusion cell in conjunction with a thermobalance. From isotherms he was able to establish phase boundaries from the weight change of his cell. Blackburn especially thoroughly examined the orthorhombic phase boundary. He found the boundary to be 2.60 at temperatures to 1100 °C and to be non-temperature dependent, in support of Biltz and Muller.

Blackburn also established the phase region for U₄O₉ and found that it can exist as a narrow region above 700 °C on either side of the composition 2.25. With the exception of the U₃O₈ boundary, Blackburn was in good agreement with Gronvold. Simultaneously with Blackburn's
investigation, Aronson and Belle\textsuperscript{15} were studying the $\text{U}_2$ phase by means of an EMF cell. This cell was composed of uranium oxide of a known composition in contact with an electrolyte which passed only oxygen. The electrolyte employed was calcia-zirconia solid solution. The standard electrode was a mixture of Fe and FeO. Using the relationship: $\Delta G = -nFE = -RT\ln P$. They were able to determine oxygen pressures at values not possible by direct techniques. In general, they agreed with extrapolations of Blackburn's curves, and found the $\text{U}_4\text{O}_9$ phase by this technique in substantiation of Gronvold. Ackermann and Thorn\textsuperscript{16} determined dissociation pressures and agreed with Blackburn except they showed that the $\text{U}_4\text{O}_9$ phase region did not exist at $O/U$ ratios above 2.25.

Ackermann, et al.,\textsuperscript{17} determined vapor pressures over $\text{U}_3\text{O}_8$ in one atmosphere of oxygen and in air. They calculated the free energy of formation of $\text{U}_3\text{O}_8$ from thermochemical data and showed this value to be in very good agreement with the one Blackburn calculated based on his and Biltz and Muller's data. In addition, they combined the vapor pressure values obtained in one atmosphere of oxygen with the free energy value for $\text{U}_3\text{O}_8$ and calculated the free energy of formation of gaseous $\text{U}_3$.

Yet to be published are the results of an investigation by Roberts and Walter\textsuperscript{18}, who have extended the range of temperature over which dissociation pressures have been determined. Dr. Roberts has graciously allowed the author to use the data obtained in his investigation prior to its publication in the Journal of Inorganic and Nuclear Chemistry.
Their investigation was in agreement with Biltz and Muller, Blackburn, and Ackermann and Thorn. They agree with the latter investigators that the $\text{U}_4\text{O}_9$ phase does not exist at $\text{O}/\text{U}$ ratios above 2.25.

Recapitulation

Although the present section concerning literature on the uranium oxide-oxygen system is by no means an exhaustive one from the standpoint of all that has been published, it does contain all the references to experimental programs which are pertinent to this current investigation. Low temperature oxidation studies, some of the structure analyses, and investigators who have only considered a small temperature or pressure portion of the system have not been discussed, as has none of the data in the literature which is obviously erroneous through misinterpretation or failure to consider all the variables such as composition changes upon quenching. A much more thorough review can be obtained from the book, Properties and Nuclear Applications,\textsuperscript{3} Chapters five and six.

For the present investigation the pertinent information needed concerns high temperature equilibrium and thermodynamic properties. Basic to this investigation, then, is the work of Biltz and Muller, Brewer, Gronvold, Blackburn, Aronson and Belle, Ackermann and Thorn, and Roberts and Walter. These authors are in accord on nearly all facets concerning the uranium oxide-oxygen system. In the few points where there is disagreement, at least two of the investigators concur on the point of contention. The results of these investigators will be considered more fully in a later section.
THEORY

Vapor pressure can be defined as the pressure which the vapor exerts on the walls of a confined system when the system is in thermodynamic equilibrium. The real significance of vapor pressure lies in the thermodynamic equilibrium. It is in this equilibrium that allows the use of vapor pressure investigations as a means of determining properties of the condensed phase.

The following section is not based on any one particular thermodynamic text nor are any proofs given concerning the laws of thermodynamics or derivations based on these laws. To do so would entail duplicating a thermodynamic text, and rather than do this, an attempt has been made to show qualitatively how the laws and derivations from them may be applied to determine the thermochemical properties of materials at high temperatures.

The notation used in this and following sections conforms to the conventions established by the International Union of Chemistry and are those used in nearly all scientific journals that have established nomenclature, with the exception of those published under the auspices of the American Chemical Society. The main difference of notation of importance in the present development concerns the usage of $G$ for free energy rather than the $F$ made so popular in this country by Lewis. It is expected that $G$ will become truly universal in the near future.

11
The Laws of Thermodynamics

There are four laws of thermodynamics, the zeroth, first, second, and third. The zeroth law is perhaps the simplest in that it merely states that if A is in thermal equilibrium with B and B is in thermal equilibrium with C, then A is in thermal equilibrium with C. It is from this law that the basis for temperature determining devices are based.

The first law merely states the law of conservation of energy. In differential form it may be written, for a chemical system,

$$\text{d}U = \text{d}q - p\text{d}V$$  \hspace{1cm} (1)

This states that the change in internal energy is a function of the work done (p\text{d}V) and the heat \text{d}q. It must be noted that \text{d}q is not an exact differential; hence, is not independent of the path over which the internal energy change occurs. An extensive treatment of this non-independence, and the implications, have been written by Slater. The quantity $U + pV$, which is related to the heat and can be determined from the heat release of a reaction, is defined as enthalpy, H, thus

$$H = U + pV$$  \hspace{1cm} (2)

The second law is much more abstract than the first and can be stated many ways. One is this: It is not possible to transfer heat from a cooler body to a hotter body without having other compensating changes occurring in the system. This is an empirical law but has never been contradicted. Based upon this law, a function is defined such that

$$\text{d}S = \frac{\text{d}q}{T}$$  \hspace{1cm} (3)
for a reversible change, and is larger than this value for an irre-
versible change. The present treatment deals only with reversible
changes. The first law becomes with (3) substituted in (1)
\[ dU = TdS - pdV \]  
(4)

Defining a function \( G \) as
\[ G = H - TS \]  
(5)

Substituting (2) into (5) and differentiating
\[ dG = dU + pdV + Vdp - SdT - TdS \]  
(6)

Substituting (4) into (6) gives
\[ dG = - SdT + Vdp \]  
(7)

It can be seen that at constant temperature and constant pressure
\[ dG = 0 \]  
(8)

This is the condition for chemical equilibrium, that for all possible
reactions the change in \( G \) be zero at constant temperature and pressure.

Imposing a constant temperature and considering one mole of an
ideal gas,
\[ dG = RT \frac{dp}{p} \]  
(9)

Integrating,
\[ G_1 - G_2 = RT (\ln p_1 - \ln p_2) \]  
(10)

If the change occurs from some standard state such as one atmosphere
pressure, then the change in \( G \) simply equals \( RT \) times the natural
logarithm of the pressure. The temperatures are in degrees Kelvin and
\( R \) is the gas constant. Lewis has generalized the above by introducing
the activity, \( a \), which makes the above equation valid when condensed
systems are involved. By considering all possible changes in a reaction and summing over the activities, he has shown that

\[ \Delta G^\circ = RT \ln K \]

(11)
The \(^\circ\) refers to the fact that the change in \(G\) is the standard free energy change. This equation (11) is of paramount importance in chemical thermodynamics and forms the basis for the present investigation in that it affords a means to determine the standard free energies of formation of non-stoichiometric systems, which is something which ordinarily cannot be done.

Little use of the third law is made in the present work, except that the entropy calculations are based on this law. The third law may be stated that for a pure crystalline material the entropy is zero, at absolute zero. Another common statement of this law is that it is not possible to attain absolute zero in a finite number of steps.

**Application of Thermodynamics to Uranium Oxide**

The above treatment leading to the relationship between the free energy change and the equilibrium constant can be applied when the activities of the various components are known. A crystalline solid where there is no solid solution has unit activity, thus is not a factor in the equilibrium constant. Under conditions where the ideal gas concept is a good approximation to a real gas, such as at high temperatures and low pressures, the partial pressure may be substituted for the activity. Considering the reaction
\[ \frac{1}{3} \text{U}_2\text{O}_8 = \text{U}_2\text{O}_3 + \frac{1}{3}\text{O}_2 \]  
\[ K_p = p_2^{1/3} \]

At 1000 K the free energy change for this reaction is about 14,400 cal/mole, and at 1500 K is 9,700 cal/mole. At this higher temperature the equilibrium constant predicts that the dissociation pressure would be about $3 \times 10^{-4}$ atmospheres. Experimentally, it is found that $\text{U}_3\text{O}_8$ loses oxygen even in one atmosphere of pure oxygen at temperatures below 1500 K. The reason for this apparent discrepancy is that the reaction (12) is not the one that occurs. The reaction best explaining the reaction actually occurring is

\[ \text{U}_3\text{O}_8 = \text{U}_2\text{O}_3 + \text{O}_2 + \frac{dx}{2} \]  

In this case, $dx$ is a true differential and is infinitesimal. In a case such as this (11) is not applicable and (10) must be used. In this case the notation is slightly changed from the way (10) is written as

\[ \bar{U} = RT \ln p \]

\( \bar{U} \) is the partial molal free energy and may be defined as the free energy change which occurs when a mole of oxygen is dissolved in a sufficiently large quantity of oxide that the composition of the oxide remains virtually unchanged. As can be seen, this adequately describes what is occurring in (12a). Integration from some state for which the free energy is known along the path of the partial molal free energy versus composition curve then may be used to arrive at an integral value for the free energy. The temperature versus composition integration since that was a requirement in the derivation of (10). Generally, it is not possible to determine the partial molal free energy completely across
the composition range, hence, an extrapolation must be made. The accuracy of the integral values are markedly dependent on how reliable this extrapolation is.

**Standard Free Energies from Vapor Pressures**

A general equation for vaporization of uranium oxides may be written

\[ \text{UO}_2: x + \frac{1-x}{2} \text{O}_2 = \text{UO}_3(g) \]  \hspace{1cm} (14)

As can be seen, this states that a reaction occurs such that a crystalline solid, \( \text{UO}_2 \), reacts with an oxygen gas to yield a volatile oxide of known stoichiometry. Equation (11) is applicable and standard free energies may be obtained. The equilibrium constant is

\[ K_p = \frac{p^{\text{UO}_3}}{p^{1-x}{\text{O}_2}^{2}} \]  \hspace{1cm} (15)

This means that at any temperature RT times the natural logarithm of the above quotient is equal to the difference in free energy between the \( \text{UO}_3 \) gas and the condensed phase. Once a value for the free energy of \( \text{UO}_3 \) has been established, using this in conjunction with the equilibrium constant allows for determining the free energy of the condensed phase wherever (14) is applicable, without the necessity for the solution approach. Conversely the establishment of standard free energies allows a means to predict the path the partial molal free energy would follow. Use of this is made in determining the pressure-temperature-composition diagram.
Of the various methods available for determining vapor pressures at high temperatures, only the transpiration method seems to be applicable when an atmosphere must be maintained to provide a reactant gas or to stabilize a phase. This can be seen by consideration of the other two methods of determining vapor pressures at elevated temperatures, the effusion method and the evaporation method.

The effusion method, by which most of the available data concerning refractory materials has been obtained, utilizes a cell in which the vapor is in equilibrium with a condensed phase. In one end of this cell there is a small orifice through which the vapor effuses. The orifice must be sufficiently small so that the vapor remains in equilibrium with the condensed phase during its effusion of the orifice. If the orifice is very small, the rate of flow out the orifice would be very slow and very long times would be required to obtain sufficient change in the cell to be detected. The condition that the mean free path be large with respect to the diameter of the orifice effectively places an upper limit of about $10^{-3}$ atmospheres on pressures that may be determined by this technique. This limitation renders this method of little use in determining equilibria where a partial pressure of reacting gas higher than $10^{-3}$ atmospheres is required.

The evaporation method suffers from the same drawback in that it only operates unambiguously in a high vacuum. This method relies on the principle that the evaporation rate per unit area is a calculable function of the vapor pressure. The presence of a gas film causes a
reduction in the evaporation rate due to collisions with the gas film in the neighborhood of the surface.

The transpiration method does not suffer from the same limitations as the above method, but does have limitations in that equilibrium must be maintained under flow conditions. While this is considered one of the major drawbacks of this method, flow rates of several cm$^3$/min may be employed and saturation maintained. The most serious drawback to this method is considered to be the necessity for a reliable means to assay the amount of vapor collected during the run. It is this factor rather than any inherent reason which fixes the range of vapor pressures over which this method may be employed.

The Transpiration Apparatus and Its Operation

The transpiration method of measuring vapor properties may be considered to be simply a probe capable of sampling gas at a specified temperature, a device for determining the total flow of noncondensable gas through the probe, a manometric device to determine the total pressure in the neighborhood of the probe, and as previously mentioned, a means of assaying the amount of condensate collected. In addition, suitable temperature control and measuring devices are necessary.

A specific apparatus that proved successful at lower temperatures formed the basis for the first transpiration apparatus employed in the current investigation.22
Initial Transpiration Apparatus

The first transpiration apparatus utilized an 18 inch platinum tube as the probe, or condenser as it is commonly called. This tube was 1/4 inch O.D. with a 0.035 inch wall. The tip of the condenser was spun shut and then drilled to put a 1/16 inch orifice for the carrier gas and vapor to enter. The total gas flow was determined with a precision model wet test meter. The uranium oxide charge was in a platinum boat with about 8 cm$^2$ surface area. The O.D. of the boat was slightly less than one inch so that it could be placed in an impervious mullite tube 30 inches long with one inch I.D. This mullite tube was placed inside a horizontal 18-inch long tube furnace which had an I.D. of 2 inches. This furnace used a nichrome heating element wound on an alumina tube and was capable of sustained operation at a temperature of 1050 C. Temperature control was effected by means of a Brown Electronik controller-recorder in conjunction with a chromel versus alumel thermocouple. The tip of the thermocouple was located in the center of the furnace in the annular space between the mullite tube and the tube upon which the heating element was wound. Controlling out in this space was found to be more effective than inside the mullite tube. Temperatures were determined with a platinum versus platinum-10 rhodium thermocouple that had been calibrated at the gold point. The emf from this thermocouple was determined with a Leeds and Northrup type K-2 potentiometer. The tip of this thermocouple was located a sixteenth of an inch from the center of the furnace and along the axis of the mullite tube. The condenser was inserted in the opposite end of the
mullite tube and was spaced a similar distance back from the center of the furnace. A rubber stopper with three holes was placed in the end of the mullite tube in which the thermocouple was inserted, one hole being for the thermocouple, one for the inlet of carrier gas, and one for a manometer. The manometer which indicated the pressure in the mullite tube was of the open end type and was filled with dibutyl phthalate because of its low density and low vapor pressure.

**Initial Transpiration Determinations**

Prior to first vapor pressure determinations, an analysis was performed on the uranium dioxide. This oxide was Mallinokrodt reactor grade, depleted in U-235. A spectroscopic examination of the sieved -200 mesh powder indicated the following impurities:

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>20 ppm</td>
</tr>
<tr>
<td>Ti</td>
<td>25 ppm</td>
</tr>
<tr>
<td>Si</td>
<td>60 ppm</td>
</tr>
<tr>
<td>Ca</td>
<td>50 ppm</td>
</tr>
<tr>
<td>Na</td>
<td>10 ppm</td>
</tr>
</tbody>
</table>

In an effort to determine to what extent the as-received powder had oxidized, an experiment was performed to determine the O/U ratio of the oxide. Use was made of the analytical procedure that regardless of the oxidation state, heating in air to about 775 °C results in stoichiometric $\text{U}_3\text{O}_8$. 
A charge of the oxide was weighed into a platinum crucible and then placed in a muffle furnace maintained at 775 C. After one hour the crucible was removed and placed in a desiccator to cool. Upon cooling, its weight was recorded and it was placed again in the furnace. This procedure was repeated three times and then the charge was left in the furnace overnight. Comparison of the weight changes indicated that over 99 per cent of the weight change had occurred on the initial firing. The analysis indicated that the initial composition of the oxide was Ud.019.

For the first experimental determination a charge of 12 grams of the dioxide was employed. The carrier gas was selected to be oxygen at one atmosphere. The gas flow rate was 15 cc/min. Initial temperature for the run was 1021 C. After running two hours with a flow of 15 cc/min the condenser was removed, cleaned on the outside, and weighed on an analytical balance. Comparison of this weight with the initial weight of the condenser prior to beginning the run indicated that a net weight loss had occurred rather than a gain, as would be predicted if vapor was condensing inside the condenser tube. The only phenomenon which would account for a weight loss was that platinum was being lost from the condenser at a faster rate than vapor was being condensed. The condenser was then washed in hot dilute nitric acid to remove the uranium condensate. No appreciable weight change was detected after this acid wash.

A similar run was performed only the time was doubled to four hours. Again a weight loss was detected rather than a weight gain. The nitric acid wash indicated a further loss, but this was only 0.1 mg.
which cannot be considered significant on an analytical balance. Since
1050 °C was about the maximum temperature attainable in the furnace, it
was decided that further work in this range of temperature would be
fruitless. A second apparatus was constructed, similar in principal to
the first but utilizing a platinum alloy wound furnace.

Second Transpiration Apparatus

Use of a platinum resistance furnace extended the temperature
range of operation to over 1400 °C. Very few changes were required in
the materials of construction since the ceramic and most of the metallic
materials were capable of operation to even higher temperatures. The
chromel versus alumel control thermocouple was changed to a platinum
versus platinum-10 rhodium thermocouple. This change necessitated
replacing the Brown controller by one capable of operating with the
smaller emf output of the noble metal thermocouple. A Foxboro model
4041 was employed as a controller. This instrument is designed for an
on-off cycle, but it was found that proper temperature control could
not be maintained in this manner so a set of resistors, themselves in
series-parallel were placed in parallel with the furnace resistance
element. This allowed for variation of the amount of current passing
through the furnace on the controller's off cycle to be varied. It was
found that a value of about 75 per cent of the current passing through
the furnace during the off cycle produced the best temperature control,
limiting the temperature cycle to less than 2 degrees centigrade. Prior
to beginning the determinations with this apparatus, a table was
constructed showing the vapor pressure and the expected weight expressed
as uranium per 1,000 cc's of carrier gas. A uranium weight was used rather than an oxide at this time, since it was not known with great certainty just what the vapor species may be.

It was considered that this table would prove of value in determining flow rates and time necessary for runs, and indicating whether it would be possible to merely weigh the condenser or if a more elaborate analytical technique would be required.

This was soon answered in that the first run at 1200 C again indicated the net weight loss that had been previously encountered. An examination of analytical techniques for determining uranium indicated that a colorimetric technique was available for determination of milligram quantities. This procedure, however, required nearly as much uranium condensate as direct weighing. The choice of analytical techniques for smaller quantities of uranium were either alpha particle counting, or use of fluorescence techniques. The fluorescence technique was selected mainly because it did not necessitate use of enriched uranium with the attendant radiation hazard. The fluorescence technique utilizes the principle that uranium in the plus six valence state fluoresces under ultra-violet light. This fluorescence beam impinges on a photomultiplier tube which converts the intensity of light to a voltage. This voltage is read on a potentiometer and from a knowledge of the voltage output of standard solutions the amount of uranium in solution may be calculated. This technique can be used to determine uranium quantities present at levels of a microgram and was found satisfactory for all the determinations employed in this investigation.
<table>
<thead>
<tr>
<th>Vapor Pressure, $\text{atm}$</th>
<th>Vapor Volume, $\text{cc}$</th>
<th>Weight Uranium, $\text{gram}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-1}$</td>
<td>100</td>
<td>-1.064</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>10</td>
<td>0.106</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>1</td>
<td>0.011</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>0.1</td>
<td>0.001</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>0.01</td>
<td>0.0001</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>0.001</td>
<td>0.00001</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>0.0001</td>
<td>0.000001</td>
</tr>
<tr>
<td>$10^{-8}$</td>
<td>0.00001</td>
<td>0.0000001</td>
</tr>
</tbody>
</table>
While the above apparatus was used for the majority of
determinations of vapor pressures made in this investigation, it does
not have the broad capabilities of the last apparatus; thus a detailed
description will be postponed until this last apparatus is described.

Third Transpiration Apparatus

In the equipment described previously a furnace was adapted
to the apparatus. In the apparatus now to be described the converse was
true. A furnace which utilized an 18 inch long silicon carbide tube as
a resistance element was the central piece of equipment about which the
transpiration apparatus was assembled. This furnace employed a zirconia
tube surrounding the silicon carbide element. Although this zirconia
had been stabilized, thermal cycling caused spalling and when zirconia
particles came in contact with the silicon carbide, a hot spot developed
and the heating element failed. For this reason it was necessary to
operate the furnace with the axis of the heating element in a vertical
position. The only change this required was that the condenser be
inserted through the top rather than the open end, as previously. Use
of this furnace increased the temperature capability to in excess of
1500 C. Since the charge was maintained in a vertical tube in this
arrangement the flow rates of gases were reduced due to the reduction in
the surface area of the uranium oxide. No attempt was made to determine
the upper limit at which saturation could be maintained. That saturation
was maintained at the flow rates employed was determined by the agreement
of the data obtained in this apparatus as compared to the previous
apparatus.
Fourth Apparatus

In an effort to expand the temperature capability to 2000 K and above, and develop a more versatile tool capable of operation under a wider range of conditions, and utilizing some of the experience gained from previous work, a fourth apparatus was constructed. Basically, this was similar to the second apparatus in that a horizontal furnace tube was used. The main improvements consisted of employing a molybdenum resistance furnace, high rhodium, platinum-rhodium alloys, improved radiation shielding, improved thermocouples, all alumina ceramics, and an improved temperature profile in the furnace.

The furnace consisted of 14 gage molybdenum wire wrapped 10 turns to the inch on a machined Morgan RR grade alumina tube. This tube is 24 inches long, 2 inches OD, and 1-1/2 inch ID, and is wrapped over 8 inches in the center. The molybdenum is held in place by Norton high-alumina cement. Insulation surrounding the cemented resistance element is bubble alumina. A Norton RA-36 Alundum tube 5 inches in diameter is coaxial with the Morgan tube. It serves to contain the alumina insulation and is the load bearing member in the furnace, keeping the weight of the additional insulation off the Morgan tube, thus preventing sagging at the elevated temperatures. A stainless steel jacket 12 inches in diameter forms the outer shell of the furnace. The space between the Alundum tube and the stainless jacket is filled with Johns Manville Superex insulation. Stainless steel end plates fastened to the jacket by means of a gasketed flange also have a water cooled O-ring seal to the Morgan tube. While the furnace was not designed for
vacuum operation, it can be evacuated to less than a millimeter. Hydrogen is introduced at both end and in the middle through holes in the Alundum tube to form a protective atmosphere for the resistance element. A flow rate of hydrogen of about 1.5 cuft/hr was found to be adequate to protect the element at temperatures over 1700 C. Power is supplied by a 220 volt, 50 amp Powerstat. At 1700 C about 22 amps and 140 volts are required to maintain constant temperature. The current is led through the stainless steel jacket by means of Conax seals. A detailed drawing of the furnace is shown in Figure 1.

The tube used to contain the condenser and charge was changed from umullite to Morgan RR alumina. This tube is 36 inches long, one inch ID with 1/8 inch wall. This use of alumina eliminates one of the potential sources of contamination, that of silicon which can occur if neutral or reducing conditions exist inside the reaction zone. The condenser selected for this apparatus was a Pt-70, Rh-30 alloy with a melting point well in excess of 1800 C. Both the wall thickness and the diameter were reduced over the previous condenser. This condenser is 22 inches long, 1/8 inch OD, and has an 0.20 wall. The main reason other than cost for the reduced diameter was that the condenser can form a major heat leak from the high temperature zone, and reducing its size minimizes this effect.

The charge was still contained in a boat, but rather than being made of elemental platinum, the boat was formed of Pt-60, Rh-40 alloy. This boat was 3 inches long and its diameter such that it would fit snugly inside the Morgan tube. Surrounding the boat and extending for one-half inch on either end was a sleeve made of the same material
FIGURE I. MOLYBDENUM WOUND, RESISTANCE FURNACE
as the boat. This served not only as a radiation shield but to protect and separate the alumina from the atmosphere as well as the charge. In both ends of this sleeve circular radiation shields of the alloy were inserted. These were formed so that a fairly tight fit with the sleeve was obtained. With this arrangement, except for a hole in either circular shield for insertion of the thermocouple and the condenser, the charge was maintained in a hollow metal cylinder to approximate a black-body as well as could be experimentally obtained.

Two additional radiation shields were spaced at two-inch intervals behind the shield that was in contact with the circular sleeve surrounding the boat. These shields were supported in an upright position by being backed with alumina disks. The disks were in turn cemented to a Degussitt alumina tube with a 1/4 inch bore. This tube ran the length from the sleeve to the rubber stopped in the end of the Morgan tube. This central tube served not only to support the radiation shields but also afforded a means to center the condenser and the thermocouple along the axis of the Morgan tube. Details of the shield assembly are shown in Figure 2.

As a means of obtaining a thermocouple capable of sustained operation at 1700 C a 60-Pt, 40-Rh versus 80-Pt, 20-Rh, was selected for use as a temperature measuring device. This thermocouple may also be used intermittently above 1800 C. The thermocouple wire was obtained from Engelhard Industries and was certified to be chemically pure. An equation expressing the temperature versus EMF was included with the wire but it was stated that the uncertainty in applying the equation to a given batch of wire was much greater than with standard compositions.
FIGURE 2. DETAILS OF REACTION ZONE
which they furnish. In an effort to determine the relationship between EMF and temperature, the thermocouple was calibrated against a calibrated Pt versus Pt, 10-Rh thermocouple. This calibration was effected by using a four-hole alumina tube and stringing both the reference and new thermocouples through this tube. The tip of this tube was imbedded in high purity alumina powder maintained in a closed-end alumina tube. The whole assembly was placed in the silicon carbide furnace and the extended thermocouple wires placed in pools of mercury maintained at the ice point in Dewar flasks. Copper leads ran from the flask to a switch so that the EMF of either thermocouple could be determined by the K-2 potentiometer. In performing the calibration, the temperature was stabilized until the EMF of the reference thermocouple changed no more than 0.2 microvolts in a five minute period. Generally, about thirty minutes were required to achieve this state at each of the temperatures at which a determination was made. The results of this calibration as well as the equation supplied with the wire and a value given in a recent publication are shown in Figure 3. An equation which expresses the results of this calibration is: 

\[ T, \text{C} = 231.84 \cdot E + 748.0. \]

A further check of the thermocouple was made by comparing the temperature indicated by the thermocouple of the molybdenum furnace with a Leeds and Northrup optical pyrometer. In this experiment the thermocouple was centered in its position inside the sleeve and above the boat. The pyrometer was sighted down the Degussitt tube with the condenser removed. Readings made by the two devices agreed to \( \pm 5 \text{ C} \). The fact that the thermocouple was visually indistinguishable lends support to
FIGURE 3. CALIBRATION CURVES FOR 60 Pt-40 Rh vs 80 Pt-20 Rh THERMOCOUPLE
the approximation of the center section of the reaction tube to a blackbody. Moving the thermocouple from one end of the boat to the other indicated that temperatures were constant to about 6 degrees at 1700 C.

Gas Flow System

Tank gases were the source of the carrier gases used in this investigation. These gases were purified prior to use in the experiments to remove possible contaminating gases which might react with the uranium oxides and mask the effect under investigation. Most care was spent in purifying tank argon which was purified by running over Drierite for water, Ascarite for CO₂, hot CuO for hydrogen, hot Cu, and finally, hot U for oxygen.

Oxygen-containing carrier gases were treated similarly except for the Cu and U getters. The hydrogen was passed over hot copper, Ascarite, and Drierite. In cases where water vapor was added to the gas, the water was deionized, boiled, and then cooled with an Ascarite trap on the gas inlet so that CO₂ would not re-enter during cooldown or in between runs.

A flowmeter was connected between the gas supply and the apparatus for purposes of indication only. This meter was a simple capillary type. During a run its main function was to insure that a constant flow rate was maintained.

With construction of the fourth apparatus, the wet test meter was discarded in favor of a water displacement type of carrier gas
measuring method. The main purpose for this change was that the gas
which passed through the condenser was retained in case further analysis
of its composition or the change of composition was to be checked.

Aspirator bottles were used to collect the gas. These were
large bottles with a tublature on the side near the bottom. Gas is
introduced through a tube running through a stopper in the top of the
bottle and down nearly to the bottom. A rubber tube is connected to
the tublature and it is through this tube that the water displaced by
the gas flows to a weighing bottle. Introduction of the gas in the
bottom serves two purposes, first it assures that the gas becomes
saturated with the water and, second, it allows the tip of the tube to
remain at atmospheric pressure during the run. If atmospheric pressure
is maintained at the bottom of the flask, this means that the gas
collected is less than atmospheric by the difference in height between
the water level in the bottle at any time and the tip of the gas delivery
tube. A manometer communicating with the gas volume allows for deter-
mination of the pressure of the saturated gas in the bottle. A
precision thermometer capable of readings of 0.1 C is also in the gas
volume for temperature determinations. The tublature at the bottom
through which the water flows also contains a standpipe so that water
can be added in the bottom and gas displaced out the top. This feature
was used in making determinations with gas mixtures. By simply putting
the required volume of reacting gas and inert gas, any partial pressure
of reactant gas could be employed for runs. To insure a constant flow
of gas out of the aspirator bottle, water was added to the standpipe at
a constant rate by means of gas displacement from another aspirator bottle. A third aspirator then displaces water with gas and the water from this bottle is weighed. As can be seen, runs using gas mixtures are considerably more complicated in that two different gases are flowing at one time, and three different aspirator bottles are changing their water volume, two are decreasing in water content while one is increasing. A line drawing of the apparatus is shown in Figure 4.

Special Procedures

It is considered that the special precautions required during some of the determinations would be more meaningful if considered in a section where the data were being discussed. One procedure entirely different from transpiration that was employed in this investigation was a thermogravimetric analysis of the oxide in air. Actual results will be considered in the section dealing with the phase diagram, but the experimental procedure will be discussed. This particular experiment was performed in air in the silicon carbide furnace. The experimental set-up was simply an analytical balance with a hole drilled through the bottom of the case so that a suspension could be attached. The suspension was a 26 gage Pt wire to which was attached a 25 ml Pt crucible. A thermocouple immediately below the crucible and one to the side and slightly above completed the apparatus.

In an effort to determine if a "chimney effect" or some other problem might arise to mask the observable weight changes, a run was performed on zirconia. Zirconia, obtained from National Lead Co. was
FIGURE 4. THE TRANSPIRATION APPARATUS
heated to 1500 C, rapidly cooled, and placed in a desiccator. Ten grams of this zirconia was then weighed on another analytical balance and then attached to the suspension and lowered into the furnace which had been maintained at 800 C. Periodic weighings were made as the zirconia was heated to 1500 C. The total weight change observed was 2 mg. The crucible was removed from the furnace and allowed to cool and reweighed on the same analytical balance initially used. This weighing indicated that 1 mg had been lost. If any effects were present which would affect the weight change, it was apparent they were no more than 1 mg in value. Temperatures were not quite so easily determined, due to the necessity for having the top of the crucible exposed to ambient temperature due to the need for a free suspension. The top thermocouple was almost uniformly 25 C cooler than the bottom one. This is probably the uncertainty in the temperature measurements, but the lower temperature value was used in plotting the data.

The run using U3O8 was performed with a charge of 9 grams and any uncertainty due to the apparatus would affect the observed O/U ratio in the third decimal place. Temperatures were considered no more accurate than 25 C, due to the necessity of maintaining the top of the crucible unshielded from a direct view of ambient temperature.
RESULTS AND DISCUSSION

Vapor solid equilibria were determined for three regions in the uranium oxygen system, the monophasic U₃O₈ region, the two-phase region between the U₃O₈ phase and the UO₂ phase, and in the UO₂ phase region. This also was the chronological order in which the investigation was made, and is the order of increasing difficulty with the experimental techniques. Each of these particular regions yielded different types of information in the present analysis. From the equilibrium with U₃O₈ the free energy of formation of UO₃(g) was established. The two-phase region supplied the information necessary to determine the pressure-temperature-composition relationships for the system when used in conjunction with existing data. The investigation in the UO₂ phase region established that UO₃ can evaporate from essentially stoichiometric UO₂, where according to Brewer, the activity of UO₃ should become quite small.

The U₃O₈ Region

Vapor pressures were determined for U₃O₈, hereinafter designated as UO₂.67 in one atmosphere of oxygen, CO₂-free air, 0.038 atmosphere O₂, and 0.0092 atmosphere O₂. In the last two cases argon was employed as a diluent to establish the total gas pressure at one atmosphere.

In pure oxygen seven vapor pressure determinations were made and are shown in Figure 5. The least squares equation representing this datum is

\[ \log p \ (\text{atm}) = -17.457 + 6.3211 \left( \frac{T}{K} \right) \]  

(16)
FIGURE 5. VAPOR PRESSURE IN ONE ATMOSPHERE OXYGEN
An error analysis indicated the probable error, and the slope and the intercept were slightly less than one per cent. Little use of such precision can be made since these data must be combined with so much other data to yield free energies of formation. It is considered that the free energies presented herein are accurate to two per cent, based on the precision possible in the various determinations.

Since the oxygen pressure used in these experiments was one atmosphere, the equilibrium constant (15) becomes simply $p_{UO_3}$. This follows, since raising $l$ to any power still results in unity. The free energy of formation of $UO_3$ then can be determined, provided a value for $UO_{2.67}$ can be determined which is applicable over the range in which experiments were performed. The two quantities, enthalpy and entropy, are dependent on temperature in the following manner:

\[
\Delta H = \Delta H_0 + \int_0^T C_p dT \tag{17}
\]

\[
\Delta S = \Delta S_0 + \int_0^T \frac{C_p dT}{T} + \frac{l_1}{T_1} \tag{18}
\]

In the above, $C_p$ refers to the specific heat at constant pressure, while $l_1$ refers to any heat effect brought on by a phase transition. Using values of Stull and Sinke\textsuperscript{26} for $U(1)$ and $O_2$, the heat of formation of the oxide determined by Huber, Holley, and Meierkord\textsuperscript{27}, and specific heat data of Popov\textsuperscript{28}, the following linearized value for the free energy of formation of $UO_{2.67}$ was determined.

\[
\Delta G = -281.960 + 49.71T \tag{19}
\]
Combining this value with the vapor pressure determinations leads to a value for the free energy of formation of $\text{UO}_3(\text{g})$ of

$$\Delta G = -202,080 + 20.79T$$

(20)

Vapor pressure made in air yielded an equation

$$\log p = -18,438 + 6.8232$$

(21)

A plot of the points and the equation are shown in Figure 6.

At 0.038 atmosphere three points yielded the equation

$$\log p = -16,255 + 5.2652$$

(22)

At 0.0092 atmosphere the equation was

$$\log p = -15.228 + 4.8470$$

(23)

Although $\text{UO}_3$ has been considered the volatile oxide, no proof has been given that this is true. Brewer considered this to be the volatile oxide and gave an argument which tended to discount those who considered $\text{UO}_3$ volatilization not possible.

That the volatile oxide has an $O/U$ ratio greater than say, 2.5 is apparent from the increase of volatility with increasing oxygen pressure. That $\text{UO}_2.67$ is not congruently subliming is apparent from the fact that the volatility is a function of the oxygen pressure. For the congruent case this would not be true. For a simple gas molecule the possibilities would seem to be $\text{UO}_3$ or perhaps $\text{UO}_4$, or possibly some polymer based upon them as a repeating structure. That $\text{UO}_4$ is not responsible for the evaporation can be seen by considering the results obtained in air. If $\text{UO}_4$ were vaporizing, the air results would be lower than those in oxygen by 0.20-67 or would be about 35 per cent of
FIGURE 6. VAPOR PRESSURE IN AIR
those obtained in oxygen. If UO₅ were vaporizing, the values obtained in air should be about 70 per cent of those in oxygen and this is what was found experimentally. A plot of Kₚ based on UO₃ as a gaseous oxide is shown in Figure 7. It is considered that UO₃ is definitely the predominant volatile oxide over uranium oxides in the presence of oxygen. That association may occur, cannot be calculated from vapor density determinations. Considerations based on the absolute entropy and some mass spectrometric evidence¹⁷ would tend to support the monomer as the gaseous oxide. A table containing all the data obtained in this phase of the investigation is given in Table 3.

The Two-Phase Region

In order to obtain data in the two-phase region it was necessary to dissociate the higher oxide until a composition of the solid of about UO₂.₅ or less was reached. This was accomplished by first starting from a low temperature in pure argon, after first oxidizing the uranium oxide with pure oxygen. As the charge was brought up to operating temperature the excess pressure due to the thermal expansion of the gas and dissociation of the oxide was allowed to escape through a bubbler to the atmosphere. It was not assumed this treatment was sufficient to insure that the two-phase composition was reached. From a consideration of the system volume and the different temperatures the different parts of the system attained during operation, it was concluded that there was a good chance the two-phase region had not been reached. A quantity of argon equal to four times the system volume (400 cm³) was passed over the charge in a reverse manner, that is, entering the
Figure 7. Equilibrium Constant, $\frac{\text{PuO}_3}{\text{PO}_2^{0.18}}$ for $\text{U}_3\text{O}_8$ Phase

Solid line is that determined in one atmosphere oxygen.
### TABLE 3. DATA OBTAINED FOR THE U$_2$O$_3$ REGION

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Flow Rate, cc/min</th>
<th>Vapor Pressure, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxygen, one atm</td>
<td></td>
</tr>
<tr>
<td>1415</td>
<td>45.2</td>
<td>9.77 x 10^{-7}</td>
</tr>
<tr>
<td>1513</td>
<td>41.9</td>
<td>5.91 x 10^{-6}</td>
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<td>1567</td>
<td>38.8</td>
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<td>12.8</td>
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<tr>
<td>1588</td>
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<td>5.71 x 10^{-5}</td>
</tr>
<tr>
<td>1760</td>
<td>4.9</td>
<td>2.61 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>CO$_2$-Free Air</td>
<td></td>
</tr>
<tr>
<td>1410</td>
<td>52.1</td>
<td>5.14 x 10^{-7}</td>
</tr>
<tr>
<td>1418</td>
<td>50.2</td>
<td>6.51 x 10^{-7}</td>
</tr>
<tr>
<td>1427</td>
<td>53.2</td>
<td>8.36 x 10^{-7}</td>
</tr>
<tr>
<td>1441</td>
<td>51.4</td>
<td>1.07 x 10^{-6}</td>
</tr>
<tr>
<td>1472</td>
<td>50.5</td>
<td>1.91 x 10^{-6}</td>
</tr>
<tr>
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<td>30.3</td>
<td>3.83 x 10^{-6}</td>
</tr>
<tr>
<td>1555</td>
<td>32.5</td>
<td>9.37 x 10^{-6}</td>
</tr>
<tr>
<td>1576</td>
<td>37.8</td>
<td>1.52 x 10^{-5}</td>
</tr>
<tr>
<td>1618</td>
<td>49.4</td>
<td>2.42 x 10^{-5}</td>
</tr>
<tr>
<td>1666</td>
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</tr>
<tr>
<td>1723</td>
<td>7.1</td>
<td>1.31 x 10^{-4}</td>
</tr>
<tr>
<td>1797</td>
<td>5.4</td>
<td>3.71 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>0.038 atm Oxygen</td>
<td></td>
</tr>
<tr>
<td>1502</td>
<td>22.0</td>
<td>2.80 x 10^{-6}</td>
</tr>
<tr>
<td>1552</td>
<td>25.1</td>
<td>6.08 x 10^{-6}</td>
</tr>
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<td>1593</td>
<td>12.7</td>
<td>1.16 x 10^{-5}</td>
</tr>
<tr>
<td></td>
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<td>3.02 x 10^{-6}</td>
</tr>
<tr>
<td>1554</td>
<td>21.8</td>
<td>4.92 x 10^{-6}</td>
</tr>
<tr>
<td>1689</td>
<td>14.1</td>
<td>9.07 x 10^{-6}</td>
</tr>
</tbody>
</table>
condenser and passing out the inlet. Use of this amount was based on Biltz and Muller's value for the dissociation pressure of 0.01 atmosphere at about 1200 °C. This amount of argon flow would reduce the O/U ratio by about 0.08 if all the oxygen came off at this value for the two-phase region. Since the dissociation pressure would be considerably higher in the monophasic region, this placed an upper limit of UO2.58 on the oxide, and probably it was somewhat less. This value was considered sufficient since the two-phase boundary appears to be slightly above UO2.60.

If the dissociation pressure in the system had been higher than 0.01 atmosphere, then the observed vapor pressures would have been higher than those obtained when the oxygen pressure was maintained at 0.0092 atmosphere, hence, an upper limit on the dissociation pressure was available. A similar procedure was employed considering the data obtained at 0.038 atmosphere.

In an effort to insure that there was no decrease in the vapor pressures with time, four consecutive runs were performed. There was some scatter in the data but no trend with time. In general, these runs were short and were run with slow flow rates, so that very little composition change would occur during a run. The data obtained in this phase of the investigation is shown with the least squares curve in Figure 8. The equation for the vapor pressure in the two-phase region is

\[
\log p = -20.370 + 7.7622 \frac{T}{1}
\]

Plotting this curve along with the other curve indicated that something was wrong with the data obtained in air. To be consistent with the phase rule would require that the curve obtained in air cross the
FIGURE 8. TWO-PHASE VAPOR PRESSURES
curve obtained for the two-phase region, but it was apparent that the curve obtained in air would cross the curve for pure oxygen first. The general procedure used in making the runs was to insert the condenser at the temperature at which the apparatus was maintained overnight (about 800°C), and then heat to run temperature under static conditions with argon present, back flow gas through the condenser to oxidize the charge, and then begin the run by reversing the flow to normal. In the case of air, this procedure was not followed. The apparatus was left open overnight to oxidize the charge, the condenser was inserted in the morning and a run begun as soon as temperature was reached and had become stable. Since in the two-phase work it was found that either argon or nitrogen gave similar results, no nitrogen-oxygen reaction could be responsible for the higher results than predicted in air. It was considered that possibly during the quick heat-up and run the oxide which was essentially UD$_2$.67 at equilibrium with 0.2 atmosphere O$_2$ at 800°C dissociated somewhat during heat-up and the actual oxygen pressure was greater than 0.2 atmosphere, which would result in higher vapor pressures. Two runs were performed in which the oxide was heated to temperature in argon, argon flowed over the charge in a reverse manner for an hour. After this treatment air flowed in the reverse manner for an hour and a half to oxidize the charge and then the run began. These values were lower than those obtained in the earlier determination and tended to clear up this discrepancy. The air curve along with these points is shown in Figure 9.
FIGURE 9. ADDITIONAL DETERMINATIONS IN AIR
<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Vapor Pressure, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Argon Carrier Gas</strong></td>
<td></td>
</tr>
<tr>
<td>1523</td>
<td>$2.90 \times 10^{-6}$</td>
</tr>
<tr>
<td>1595</td>
<td>$9.81 \times 10^{-6}$</td>
</tr>
<tr>
<td>1792</td>
<td>$1.85 \times 10^{-4}$</td>
</tr>
<tr>
<td>1850</td>
<td>$3.61 \times 10^{-4}$</td>
</tr>
<tr>
<td>1801</td>
<td>$5.21 \times 10^{-4}$</td>
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<tr>
<td>1803</td>
<td>$3.46 \times 10^{-4}$</td>
</tr>
<tr>
<td>1735</td>
<td>$8.41 \times 10^{-5}$</td>
</tr>
<tr>
<td><strong>Nitrogen Carrier Gas</strong></td>
<td></td>
</tr>
<tr>
<td>1593*</td>
<td>$9.01 \times 10^{-6}$</td>
</tr>
<tr>
<td>1594*</td>
<td>$7.90 \times 10^{-6}$</td>
</tr>
<tr>
<td>1595*</td>
<td>$9.11 \times 10^{-6}$</td>
</tr>
<tr>
<td>1597*</td>
<td>$8.25 \times 10^{-6}$</td>
</tr>
<tr>
<td>1504</td>
<td>$1.66 \times 10^{-6}$</td>
</tr>
<tr>
<td>1493</td>
<td>$2.31 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

* Consecutive runs performed with re-oxidation.
The Temperature-Pressure-Composition Diagram

Sufficient information was now available to establish a phase diagram showing the oxygen pressures necessary for equilibrium with the different phases and compositions of uranium oxide. First, however, it was necessary to establish the simpler temperature-composition diagram. Establishment of this diagram was based on an assessment of the literature and is possibly somewhat subjective as to which data to believe when apparent discrepancies exist. The diagram was based on the work of Gronvald, Biltz and Muller, Ackermann and Thorn, Blackburn, Aronson and Belle, and Roberts and Walter.

All the above investigations are in general agreement, at least at temperatures above 1000 K. A brief description of the system is as follows: a fluorite phase exists from an O/U ratio of 2.00 to about 2.20, with this phase region extending to higher O/U ratios with increasing temperature. The limiting value is about 2.24 at 1400 K but there is indication based on the yet unpublished work of Roberts and Walter that this may shift slightly to higher O/U ratios with increasing temperature. At O/U ratios from about 2.20 to 2.25 and at temperatures below 1400 K, the U₄O₉ phase exists. There is some question concerning existence of this phase above an O/U ratio of 2.25. An O/U ratio of 2.25 is regarded herein as the upper composition limit for this phase. There is some disagreement between the diffraction results and equilibrium investigations concerning the lower O/U limit of the orthorhombic phase. Both Biltz and Muller, and Blackburn found about 2.80 for this boundary and reported it to be independent of temperature.
Diffraction studies have shown that the boundary shifts to lower O/U ratios with increasing temperature. The Blackburn values are accepted on the basis of his close examination of the orthorhombic portion of the system. The temperature-composition diagram based on the above considerations is shown in Figure 10.

Construction of an isotherm for the system consisted of plotting a series of partial molal free energies, $\bar{G}$, as a function of composition. $\bar{G}$, as has previously been discussed, is the energy change in dissolving a mole of oxygen in sufficient quantity of oxide such that the composition of the oxide is unchanged. It is related to the dissociation pressure by the relation: $\bar{G} = RT \ln p_{O_2}$. The manner in which this construction was accomplished was by first establishing the free energies for the two-phase regions from dissociation pressure data. By use of the temperature-composition diagram the composition limits for the phase regions were obtained.

Aronson and Belle have shown that the change of free energy with composition is not linear. An assessment of their data indicates, however, that no gross errors would occur if the fluorite phase region were treated linearly. Figure 11 illustrates this in that the smooth curve is that based on thermodynamic values with the data of Aronson and Belle superimposed upon it.

It was concluded that a similar procedure could be used at other temperatures. From dissociation pressure determinations over the fluorite-orthorhombic two-phase region a value for the partial molal free energy could be obtained. From thermodynamic data for UO$_2$ and
FIGURE 10. TEMPERATURE-COMPOSITION DIAGRAM FOR URANIUM OXIDE
FIGURE II. PARTIAL MOLAL-FREE ENERGY VS COMPOSITION AT 1250 K
assuming a linear variation of free energy with composition, it would be possible to establish the free energy variation over the monophasic region providing sufficiently reliable data were available. The first step in accomplishing this would be to establish the dissociation pressure for the two-phase region. This not only would establish the partial molal free energy for the two-phase region, but would supply the needed ingredient in calculating standard free energies from the vapor pressure determinations carried out in the two-phase region. The vapor pressure curves obtained at fixed oxygen pressures simply state that at a fixed oxygen pressure and fixed temperature the vapor pressure has a certain value. No two vapor pressures determined with fixed oxygen pressures were made with exactly the same condensed phase. That the equilibrium plot and the free energy determination of \( \text{WO}_3 \) are possible, is due to the small energy differences associated with changes of stoichiometry in this phase region. The vapor pressures for the two-phase region were made with a constant composition and an oxygen pressure that varied. At a temperature at which the vapor pressure curve for one of the fixed oxygen curves crossed the two-phase curve, at that temperature the composition was that of the two-phase region and the dissociation pressure that of the fixed oxygen pressures. From the two-phase curve (24) and the fixed oxygen curves (16), (21), (22), and (25) by solving for the temperatures of intersection the values shown in Table 5 for the dissociation pressure were found. The value for air was corrected as has been previously discussed. These values are shown in Figure 12 along with extrapolations based on literature values.
Figure 12. Dissociation Pressure for the Orthorhombic-Fluorite Two-Phase Region
TABLE 5. DISSOCIATION PressURES FOR
THE TWO-PHASE REGION

<table>
<thead>
<tr>
<th>Pressure, atm</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2021</td>
</tr>
<tr>
<td>0.21</td>
<td>1830</td>
</tr>
<tr>
<td>0.058</td>
<td>1728</td>
</tr>
<tr>
<td>0.0092</td>
<td>1592</td>
</tr>
</tbody>
</table>

These values were considered sufficiently close to the work of Roberts and Walter to indicate that use of their value for the dissociation pressure in conjunction with the two-phase vapor pressures should lead to reliable free energy data. The free energy of the condensed phases were determined from the equilibrium constant and from the free energy of UO₃. Considering UO₂₋₆₀ to be the composition limit for the orthorhombic phase

\[ \text{UO}_2 \cdot 60 + 0.20 \text{O}_2 = \text{UO}_3(g) \]  

then

\[ \log K_p = \log p(\text{UO}_3) = 0.20 \log p(\text{O}_2) \]  

Roberts and Walter's dissociation pressure is given by

\[ \log p = -17,460 + 8.78 \frac{T}{T} \]  

Combining these leads to a value for the free energy of formation of UO₂₋₆₀ of

\[ \Delta G = -279,700 + 48.48T \]  

In an analogous manner a value for UO₂₋₂₄, considered the upper limit for the fluorite phase at about 1400 K, was found to be

\[ \Delta G = -264,900 + 41.06T \]
If the value of the boundary were $UO_{2.25}$, the free energy would be

$$
\Delta G = -266,000 + 41.35T
$$

(30)

The free energy of $UO_2$ was calculated in a manner similar to that performed by Coughlin except that the temperature range of validity of the present equation is from 1405 K, the melting point of uranium, to 2000 K. This equation in its linear form is

$$
\Delta G = -258,490 + 40.56T
$$

(31)

Equations (31), (30), (29), and (27) are all that are required to establish partial molal free energy curves from $UO_2$ to $UO_{2.60}$.

Blackburn has assessed his data and that of Biltz and Muller's and this assessment can be used to complete the curve to $UO_{2.67}$. This orthorhombic phase becomes decreasingly important at higher temperatures and with subatmospheric oxygen pressures. Since the partial molal free energy is expressed per mole of oxygen, it is necessary to write the equation so that a mole of oxygen appears. The reaction

$$
8UO_{2.25} = 6UO_2 + O_2
$$

(32)

expresses the total length of the path of the partial molal free energy from $UO_{2.25}$ to $UO_2$. Since the partial molal free energy is known and the $UO_{2.25}$ from the dissociation pressures, then if a function is assumed, it becomes a simple matter to complete the diagram. Aronson and Belle have shown at lower temperatures that while a linear behavior is not encountered the deviation from linearity is small, this is shown in Figure 11 which compares the thermodynamic treatment with Aronson and Belle's experimental data at 1250 K. The partial molal free energy curve obtained at 1600 K is shown in Figure 13 along with an extrapolation of Aronson and Belle's work. Additional curves were determined
From thermodynamic data

Calculated from Aronson and Belle

Blitz and Muller (extrapolation)

FIGURE 13. PARTIAL MOLAL-FREE ENERGY VS COMPOSITION AT 1600 K
at 1800 K and at 2000 K. From these the diagram shown in Figure 14 was derived. This diagram supplied the information necessary before an investigation of the fluorite phase could be attempted.

The thermogravimetric analysis previously mentioned which was performed in air can be compared to the behavior of the oxide predicted from the diagram. Data from Budnikov\textsuperscript{30} and Lynch\textsuperscript{31} is included and are shown in Figure 15. The agreement between experimental values and the predicted behavior is considered quite good.

**The UO\textsubscript{2} Phase**

Some data for the UO\textsubscript{2} phase have already been obtained, as was mentioned in the last section. The fully oxidized state of the fluorite phase is in equilibrium with the UO\textsubscript{3} gas in the two-phase region and has been previously discussed. Since it was shown that the free energy variation across this phase field is essentially linear and a good value for the free energy of formation of UO\textsubscript{2} exists, there is little that can be done experimentally in this phase region that cannot now be predicted from the data generated thus far. It was decided to make experimental determinations in the neighborhood of the stoichiometric UO\textsubscript{2} compositions to determine experimentally that equation (14) is applicable under conditions where the atmosphere is only slightly oxidizing or is actually reducing. Examination of the compositional diagram indicated that oxygen pressures of the order of 10\textsuperscript{-6} atmosphere of oxygen would be necessary to obtain an O/U ratio below 2.01.

With the capability of the gas mixing system about 30 liters, 0.06 cc
FIGURE 14. PRESSURE—TEMPERATURE—COMPOSITION OF URANIUM OXIDE
Figure 15. Predicted equilibrium in air compared with experimental values.
of oxygen would have to be added to the 30 liters of argon to make the required mixture. It was considered impractical to attempt to use argon-oxygen mixtures; rather it was decided to use argon-water mixtures to achieve low partial pressures of oxygen by the thermal decomposition of the water vapor.

Three runs were performed in argon on the UO₂ at 1600 °C and gave vapor pressures of 10⁻⁴ atmosphere. This was much higher than anticipated since a vapor pressure of UO₂ subliming congruently was expected. These values were several orders of magnitude higher than Aokermann's vapor pressure of UO₂, and if UO₃ were vaporizing would indicate that the oxygen content of the argon was about 50 ppm. With this much oxygen in the system, addition of water should have no effect on increasing the volatility, and performing another run with argon containing 3 per cent water vapor resulted in the same value for the vapor pressure. A mass spectrometer was then employed to determine the oxygen concentration in the gas leaving the furnace. The result of this analysis was that oxygen was detected in the gas but was below the limit for which a quantitative number could be obtained. Oxygen could be determined quantitatively to 0.01 per cent and its presence detected if there at a concentration greater than 0.0001 per cent. This verified the analysis of the high vapor pressure values in that the mass spectrometer verified that oxygen was present somewhere between 1 and 100 ppm as had been suspected. The reason for this oxygen was not known. The tank argon was passed over copper so that the oxygen content should have been 10⁻¹⁰ per cent. Whether oxygen was diffusing in through the neoprene tubing used in making connections, or passing through the
Morgan tube was not known. It was known, however, that the alumina was not impervious to any marked extent above 1600, since it was a common observation that the annular space between the two alumina tubes (the one the heating element was wound on and the one containing the charge) contained an appreciable amount of water vapor. It was considered that this water was formed by hydrogen diffusing through the tube the element was wound on and recombining with oxygen from the air in the annular space. It was observed that some of this water found itself through the inner alumina tube also.

To insure that no extraneous oxygen was in the apparatus, gas mixtures of argon, hydrogen, and water vapor were employed. Gas mixtures containing hydrogen of a few per cent were mixed over water as before and were allowed to enter the furnace in a saturated condition with respect to water vapor. With this arrangement, oxygen pressures of $10^{-7}$ atmosphere and below could be used. With the hydrogen pressure between 0.01 and 0.1 atmosphere the atmosphere in the furnace was reducing in nature.

The procedure used in the runs was to purge the system with pure hydrogen at one atmosphere pressure and then to introduce argon to remove the major portion of the hydrogen in the apparatus until the partial pressure of hydrogen was the same as the gas to be used in the run. It was not possible to determine precisely when the partial pressure of hydrogen was at the point when the run could begin. However, based on a knowledge of the system volume this time could be estimated. Rather than use values for the partial pressure of hydrogen and water
vapor in the initial gas mixture, these quantities were determined by analysis of the gas after it flowed through the condenser.

Magnesium perchlorate was used to collect the water vapor in a drying tube which could be weighed. From the weight gain and the total gas flow the partial pressure of water vapor in the gas could be determined. A sample vial was in the exit line so that samples of the gas could be determined mass spectrometrically for hydrogen content. These quantities plus the vapor pressure were required to calculate the equilibrium constant. This reaction can be considered a two-step reaction:

\[
\begin{align*}
H_2O(g) &\rightarrow H_2 + \frac{1}{2} O_2 \\
UO_2 + \frac{1}{2} O_2 &\rightarrow UO_3
\end{align*}
\] (33)

or simply

\[
UO_2 + H_2O \rightarrow UO_3 + H_2
\] (34)

In this case the equilibrium constant is given by the product of the vapor pressure of \( UO_3 \) and the partial pressure of \( H_2 \) divided by the partial pressure of water vapor. Results obtained from this phase of investigation show more scatter than in other phases of the investigation. Considering the temperature and the extreme precautions necessary to preclude oxygen, and the possibility of atmospheric reactions with materials of construction, it is considered that the data obtained is quite significant. A plot of the data expressed as the equilibrium constant for equation (34) is shown in Figure 16, and the data are presented in Table 6. The equation of the line representing the data is

\[
\log K_p = -25.000 + 7.40T
\] (35)
Figure 16. Equilibrium constant for $\text{UO}_2 \frac{\text{PUO}_3 \cdot \text{PH}_2}{\text{PH}_2\text{O}}$
<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>$p_{\text{UO}_2}$, atm</th>
<th>$p_{\text{H}_2\text{O}}$, atm</th>
<th>$p_{\text{H}_2\text{O}}$, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1826</td>
<td>$2.03 \times 10^{-7}$</td>
<td>0.0193</td>
<td>0.029</td>
</tr>
<tr>
<td>1901</td>
<td>$6.61 \times 10^{-7}$</td>
<td>0.0234</td>
<td>0.0183</td>
</tr>
<tr>
<td>1844</td>
<td>$3.32 \times 10^{-7}$</td>
<td>0.0270</td>
<td>0.0233</td>
</tr>
<tr>
<td>1965</td>
<td>$1.16 \times 10^{-6}$</td>
<td>0.0232</td>
<td>0.0824</td>
</tr>
<tr>
<td>1762</td>
<td>$4.57 \times 10^{-6}$</td>
<td>0.0290</td>
<td>0.0108</td>
</tr>
<tr>
<td>1946</td>
<td>$1.04 \times 10^{-5}$</td>
<td>0.0310</td>
<td>0.0192</td>
</tr>
<tr>
<td>1929</td>
<td>$1.07 \times 10^{-5}$</td>
<td>0.0290</td>
<td>0.0920</td>
</tr>
<tr>
<td>1785</td>
<td>$1.55 \times 10^{-5}$</td>
<td>0.0285</td>
<td>0.0732</td>
</tr>
<tr>
<td>1857</td>
<td>$7.81 \times 10^{-7}$</td>
<td>0.0322</td>
<td>0.0710</td>
</tr>
<tr>
<td>1852</td>
<td>$4.04 \times 10^{-7}$</td>
<td>0.0292</td>
<td>0.0850</td>
</tr>
</tbody>
</table>
This implies that the free energy change for reaction (34) is

$$\Delta G = 114,300 - 53.80T$$

Coughlin gives for the free energy of formation of $H_2O(g)$

$$\Delta G = -58,850 + 13.12T$$

Combining these two with the free energy of formation of $UO_2(g)$ (Equation 20)

$$\Delta G = -202,080 + 20.79T$$

The free energy of formation of $UO_2$ is found to be

$$\Delta G = -257,530 + 41.47T$$

Comparing this with the value derived from calorimetric data

$$\Delta G = -258,490 + 40.56T$$

It can be seen that very good agreement has been obtained for this phase of the investigation, the numbers being identical within the experimental error inherent in both types of determinations.
SUMMARY

Vapor pressures have been determined over uranium oxides covering a temperature range from 1400 to 2000 K. A composition limit ranging from U$_3$O$_8$ to UO$_2$ was covered in three series of determinations, depending on the nature of the condensed phase being investigated. It has been shown that such equilibria as determined herein can be used to obtain information concerning the condensed phase that cannot be obtained by direct determination of the condensed phase properties, at temperatures of interest.

Specifically, this investigation established the free energies of formation and a more meaningful phase diagram at temperatures higher than had previously existed and did it in a manner independent of previous work in the system. A free energy value for U$_3$O$_8$ was computed from literature and from an extrapolation of specific heat data. This was combined with vapor pressure data to determine the free energy of formation of U$_3$(g). Equilibrium in the two-phase region supplied the data for determining the free energy of UO$_2$.60 and UO$_2$.24 and also was beneficial in determining the dissociation pressure of this region at temperatures that preclude direct determination of this quantity. Calculation of the free energy of UO$_2$ in a manner similar to that for U$_3$O$_8$, when combined with the data obtained for the two-phase region, supplied the necessary information to establish a phase diagram showing the effect of oxygen pressure on the equilibrium oxide composition. Finally, it was established that the vaporization process responsible for the volatility of higher oxides of uranium is a means of vaporization.
for stoichiometric $\text{UO}_2$ if traces of oxygen are in the system. Free energy values applicable over the temperature range from 1405 K to 2000 K are included in the following table.

**TABLE 7. STANDARD FREE ENERGY OF FORMATION**

<table>
<thead>
<tr>
<th>$O/U$</th>
<th>$A$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3(g)$</td>
<td>202,080</td>
<td>20.79</td>
</tr>
<tr>
<td>2.87</td>
<td>281,960</td>
<td>49.71</td>
</tr>
<tr>
<td>2.60</td>
<td>279,700</td>
<td>48.48</td>
</tr>
<tr>
<td>2.24</td>
<td>264,900</td>
<td>41.06</td>
</tr>
<tr>
<td>2.00</td>
<td>258,900</td>
<td>40.56</td>
</tr>
</tbody>
</table>

The above table plus the composition diagram shown in Figure 14 supply the information necessary concerning the stability of the uranium oxides and define the system so that its behavior with other materials may be apprised. These also establish the binary system so that ternary oxide systems may be investigated to see if enhanced physical properties may be achieved by additions of other oxides to uranium. This treatment could be used as a basis for such an investigation for it is now possible to calculate the vapor pressure of uranium oxides under any condition of temperature and oxygen pressure. Experimental determination of vapor pressures would then make it possible to calculate the activity of uranium oxide in the mixed oxide. A study of this sort over a range of compositions and temperatures would result in a thermodynamic description of the ternary system and would afford possibly the only means by which the stability of possible nuclear fuels may be determined quantitatively.
CONCLUSIONS

The uranium oxide system has been investigated by a different technique than those used in the past, and by one that permits direct determination of thermochemical quantities needed for predictions concerning possible high temperature nuclear applications. The development need only depend on one extra quantity, either an independent determination of the free energy of formation of \( \text{UO}_3 \), a value for the free energy of \( \text{U}_3\text{O}_8 \), or one for \( \text{UO}_2 \). In this work the value for \( \text{U}_3\text{O}_8 \) which was developed to cover the temperature range of interest was employed. The results indicate that the value for \( \text{UO}_2 \) could have been used with the same results. This certainly implies that the free energy values contained herein are consistent, and they are consistent with the work of a sufficient number of other investigators that it must be concluded the uranium oxide-oxygen system has been defined by the free energy values contained herein and by the pressure-temperature-composition relationships derived from them and other pertinent data.

The theory and experimental techniques described herein could be applied to other systems whose high temperature properties have not yet been defined. One such application would be the iron-oxygen system. Vaporization mechanism is of considerable importance in this system because of the air pollution associated with reduction of iron ores. Vapor pressure determinations could determine the nature of the vapor species, their dependence on atmosphere, and possible additives to minimize the vapor pressure. There are undoubtedly many other systems of practical importance which could be investigated by the techniques
developed in this dissertation, and it is hoped that in the future, additional use will be made of this method to augment our knowledge of materials behavior at elevated temperatures.
REFERENCES


24. E. J. Center, AECD-3006 (June, 1948).


I, Carl Albert Alexander, was born in Chillicothe, Ohio, November 22, 1928. I was educated in the Chillicothe public school system, and was an undergraduate student prior to service in the Korean War. Upon separation from active service I received the Bachelor of Science degree in mathematics from Ohio University in 1955. In 1956, I received the Master of Science degree in physics from Ohio University. In 1957, I enrolled in the graduate school of the Ohio State University as a special student by my own request. Since 1959 I have specialized in the Ceramic Engineering Department while completing the requirements for the Doctor of Philosophy degree.