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ON THE BERKELIUM -
OXYGEN SYSTEM

March 1971

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ON THE BERKELIUM - OXYGEN SYSTEM

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PREFACE

From the work reported in this document, two papers are to be published in the open literature. These are:

- "ThermoChemical Measurements with a Capacitance Manometer" to be published in Analytical Chemistry about June 1971.
- "Oxygen Decomposition Pressures and Thermodynamic Data for Nonstoichiometric Berkelium Oxide" to be published in Journal of Inorganic and Nuclear Chemistry, about September 1971.

During the course of developing the somewhat unique apparatus used for conducting experiments on the decomposition of berkelium oxide, a number of experimental problems were encountered. It is the purpose of this report to discuss these problems in greater detail than possible in the above journal articles, and to describe solutions and/or possible interpretations for these observations. This report also serves a means for tabulating all of the experimental data generated in the berkelium oxide study.

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ABSTRACT

A unique, highly sensitive system for the quantitative measurement of decomposition pressures of small samples has been used to obtain equilibrium oxygen decomposition pressures over a 1.22 milligram sample of nonstoichiometric berkelium-249 oxide. The temperature and pressure range investigated was 852 to 1150°C and from 10^{-7} to 10^{-20} atm O_2 , respectively. These conditions were sufficient to enable examination of the entire compositional range between BkO_2 and Bk_2O_3 . Partial thermodynamic quantities were derived and found to be a function of composition but independent of temperature. The shapes of the equilibrium decomposition pressure isotherms were used to deduce the possible condensed phase relationships in this oxide system.

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ON THE BERKELIUM - OXYGEN SYSTEM

INTRODUCTION

Over the past quarter century, an unprecedented effort has been made toward an understanding of the chemistry and physics of actinide compounds. The oxides have been of particular interest, and UO_{2+x} must be among the most thoroughly studied of any solid material. The plutonium - oxygen system and transplutonium oxides have been investigated for reason of possible nuclear application and will continue to be studied as important examples of non-stoichiometric compounds. While all of the actinide oxides are isostructural at $MO_{2.0}$ (CaF_2 structure) it is clear that in detail, their behavior at deviations from stoichiometry is remarkably different.

There has been a substantial effort in this laboratory towards an understanding of nonstoichiometric behavior in these systems. Oxygen dissociation pressures and partial thermodynamic relations were determined for AmO_x ⁽¹⁾ and phase relations described for CmO_x ⁽²⁾ using a thermobalance technique on one-gram and 200-milligram samples, respectively. It is the purpose of this report to give pressure-temperature-composition results on a 1.22 mg sample of BkO_x , and to describe a unique system of high sensitivity for performing thermochemical measurements on milligram quantities of sample.

There are a number of papers which are relevant to further discussion. A general review of the literature concerning rare earth and actinide fluorite related oxides has been given by Eyring.⁽³⁾ Of the rare earth oxide systems, those of Ce,⁽⁴⁻⁵⁾ Pr,⁽⁶⁾ and Tb⁽⁷⁾ (isoelectronic to Bk) need to be considered. Of the actinides, two studies are particularly notable in that a pressure measurement technique was used to measure stoichiometry as was employed in this study. These are the work on UO_{2+x} by Roberts and Walter⁽⁸⁾ and that on AmO_x by Asprey and Cunningham⁽⁹⁾. It may be noted here that the usual thermogravimetric approach, using the Cahn electrobalance which offers a high sensitivity of $\sim \pm 2 \mu g$ under carefully controlled conditions, would lead to an uncertainty of about ± 0.04 in x for 1.22 mg of BkO_x .

Several micro-scale x-ray investigations of Bk_2O_3 and BkO_2 have been reported ^(10,11) confirming the existence of a bcc (bixbyite) sesquioxide and fcc (fluorite) dioxide. It was also reported that hydrogen reduction of the dioxide at 600°C gave Bk_2O_3 , and reoxidation to BkO_2 in air or oxygen was rapid at the same temperature.

The Bk^{249} isotope decays to Cf^{249} with a half-life of 314 ± 8 days. ⁽¹²⁾ The decay occurs primarily by beta emission (0.114 Mev) with the α/β ratio = 2.2×10^{-5} . The Cf^{249} daughter is primarily an alpha emitter and has a relatively long half-life of 360 years. By interpolation of the estimates of Kinchin and Pease ⁽¹³⁾ concerning threshold radiation energies for displacement, beta particle energies of 0.13 Mev and 1.30 Mev are necessary to displace oxygen and berkelium, respectively, from lattice sites. Since the measured energy is 0.114 Mev, very slight radiation damage to the crystal is anticipated. (It might be remarked that the high purity Al_2O_3 crucible containing the BkO_2 sample was, however, discolored [tan-orange] in the vicinity of the sample, presumably by radiation damage.)

Because the data to be discussed include compositions approaching approximately 13% Cf, a consideration of californium oxides is important. The sesquioxide, Cf_2O_3 , exists in both bcc and monoclinic structures ⁽¹⁴⁾ at low and high temperatures, respectively. Green ⁽¹⁵⁾ has reported that combustion of Cf oxalate at 1200°C in air resulted in the monoclinic modification, probably of stoichiometric composition. Copeland, ⁽¹⁴⁾ however, reports a smaller lattice constant for cubic Cf_2O_3 prepared by low temperature oxidation of CfOCl in 0.5 atm O_2 than observed for Cf_2O_3 prepared by hydrolysis of CfOCl . This suggests the presence of Cf^{+4} under these conditions. It is to be noted that the partial oxygen pressure in our oxidation experiments (7 Torr at 500°C) was a factor of greater than 50 less than Copeland's, and if Cf^{+4} is present under these conditions, its effect on the measured O/Bk values is probably negligibly small. This assumption is consistent with the results as will be discussed later. The existence of Cf^{+4} has recently been conclusively demonstrated ⁽¹⁶⁾ by the preparation of CfO_2 and $7\text{NaF} \cdot 6\text{Cf}_4$.

Ryan ⁽¹⁷⁾ has brought to our attention recent determinations of the standard (III-IV) oxidation potentials obtained through f $\rightarrow$ d adsorption band shifts and that some correspondence to relative stabilities of the (III-IV) oxides should exist. On this basis, he correctly predicted that the thermal

stability of BkO_2 would lie between CeO_2 and AmO_2 . On the basis of the general decreasing stability of the dioxide with increasing atomic number, it was previously felt that BkO_2 would be of similar (or lower) stability than CmO_2 .

In retrospect, we have been able to demonstrate an excellent correlation of standard oxidation potentials and dissociation pressures as shown in Figures 1 and 2 for $\text{MO}_{1.70}$ and $\text{MO}_{1.90}$, respectively. The latter curve also predicts dissociation pressures for actinide oxides which have not yet been measured. These plots include, in a sense, unconfirmed data since the BkO_x dissociation pressures have not been previously measured and the new oxidation potential for $\text{Am}^{\text{III-IV(17)}}$ is much higher at -2.0v than the previous value of -2.8v. Data for the lanthanides were not included since a somewhat arbitrary correction must be made to fit both series to a single curve.

It was the goal of this study to define in as much detail and as rapidly as possible (in view of the 314 day half-life), the oxygen dissociation pressures over BkO_x , derive the appropriate thermodynamic functions, and determine the phase relations in the BkO_2 - Bk_2O_3 system.

EXPERIMENTAL

Since the technique employed in this investigation is new, considerable care was taken to define inherent reproducibility and accuracy. Large portions of the following discussion deal with these areas.

The general method employed in relating the three variables P_{O_2} , T , and O/Bk involved certain basic steps, optimized so as to give maximum data per unit time. The investigation was limited to five temperatures (852, 925, 996, 1075, and 1150°C) from which much of the desired information could be obtained. Mixtures of known CO_2/CO ratio were equilibrated with the sample for ~1.3 hours. The system was then evacuated, thereby "freezing" the O/Bk ratio and the sample cooled to 500°C. Oxidation to the dioxide was carried out at this temperature, using the capacitance manometer to measure quantitatively the change in pressure due to oxygen uptake by the sample. A knowledge of the initial weight of the sample, corrected for decay, and an accurate measurement of the system volume/temperature ratio, as discussed later, allowed calculation of stoichiometry via the ideal gas law. It

FIGURE 1. Dissociation pressures versus standard (III-IV) oxidation potentials for $\text{MO}_{1.70}$ at 900°C .

FIGURE 2. Dissociation pressures versus standard (III-IV) oxidation potentials for $\text{MO}_{1.90}$ at 900°C . Open circles are experimentally determined dissociation pressures.

should be pointed out that the sample was not vacuum reduced by the evacuation step since pressures of less than $\sim 10^{-5}$ atm. were not achieved at the sample.

The heart of the system utilized in the study was a capacitance manometer supplied by MKS Instruments Inc. Although a Type 77 head was initially evaluated, problems related to an unsymmetrical design and outgassing of organic components resulted in an unacceptable long-term drift. The Type 90 head employed is a totally symmetrical, all welded unit with metal and ceramic components only. The internal volume on both sides of the head is ~ 6 cc. The capacitance manometer contains a hermetically sealed Inconel - X diaphragm, which senses differential pressure changes via an AC capacitance bridge, sensitive to deflections of 10^{-9} inches or $\sim 2 \times 10^{-7}$ Torr under optimum conditions. The unit employed had calibrated full-scale differential ranges of ± 10 , 3, 1, 0.3, 0.03, 0.01, and 0.003 Torr and could be observed via a meter or recording of the ± 100 mv dc output on each range. The 0.1 Torr range was used almost exclusively in this study and on 10 in. chart paper, pressure could be estimated to 0.1 milli-Torr.

During preliminary experiments in which pressure was monitored as a function of temperature, the decade dials were used to null accurately the manometer (and recorder) every 0.1 Torr (or 0.01 Torr). Individual pressure readings during the BkO_x study were read directly from the readout dials in the null position.

The manometer head was connected to an all stainless steel system as shown schematically in Figure 3. The tubing and bellows valves were 1/4 in. and much of the tubing volume was reduced by insertion of stainless steel welding rod. The valve system was mounted on a 1/8 in. copper plate and placed within a 15 in. x 18 in. x 8 in. copper box to which copper coils had been soldered. Coils were also soldered to the mounting plate, the manometer head being below the plate. The copper box (~ 40 lbs.) was insulated with 2 in. of styrofoam and the temperature was maintained constant at 24.8°C using a Haake re-circulating water bath employing a Pt resistance sensor.

The water circulator efficiency was improved by use of a constant level reservoir of cold tap water from which the cold coil within the Haake

FIGURE 3. Capacitance manometer system. The dashed lines represent the thermostated copper box. X and R on the manometer refer to the sample and reference sides, respectively.

reservoir was gravity fed. Temperature fluctuations of some tenths °C could still be observed using a cathetometer and precision thermometer within the bath. These were short term (~2 minutes), however, and did not appear to affect the capacitance manometer readings. Long-term stability (24.8°) of ~3 months was attained. Even though these precautions were taken, a correlation was found between manometer readings and room temperature with ≥ 400 Torr gas in the system. Even with control of room temperature to better than $\pm 1^\circ\text{C}$, at higher pressures fluctuations and/or drift over ~12 hr. periods could not be reduced to less than ± 5 μTorr . These fluctuations can be explained in terms of average temperature differences of $\sim 0.01^\circ\text{C}$ on the two sides of the system. A totally symmetrical system, shown in Appendix A, has been constructed which should eliminate much of the difficulties mentioned here.

The sample tube and crucible are shown in Figure 4. The 0.390" O.D. alumina tube was machined to an I.D. of 0.305". The crucible dimensions were 0.500" x 0.250" O.D. x 0.200" I.D. with a 0.020" clearance between the cap and the bottom of the crucible, where the sample was confined. The final tube used was larger in I.D. than planned, requiring a sleeve to fill the void between the crucible O.D. and tube I.D. The grooves cut in the cap were 0.013" x 0.15" deep. The 0.030" diameter alumina filler rod in contact with the crucible cap, had a 0.025" x 0.025" groove cut in to it to facilitate pumping and communication between the sample and bulk of the equilibrating gas. The quartz rod, placed above the alumina rod and outside of the furnace, had a diameter of 0.300".

An approximate volumetric consideration of various parts of the system is shown in Figure 5. There were several opposing requirements on volume due to the small sample available. In terms of sensitivity, the smaller the system, the better. However, the effect of the hot zone needed to be minimized by making the hot zone volume small in comparison to the total volume. Due to radiolysis of solutions of radioisotopes such as Bk^{249} resulting in a boiling-type effect, it was necessary to load the sample into a relatively large crucible (1/4 in. dia. x 1/2 in.). Also, it was desirable to ensure that gas could get to and from the sample and yet restrict the

FIGURE 4. Sample tube assembly showing crucible and slotted cap and Al₂C₃ and quartz filler rods.

BKO_x SAMPLE TUBE ASSEMBLY

FIGURE 5. Schematic of volume-temperature relations along the tube assembly with the sample at the 500°C oxidation temperature. The seal region at 15°C is water cooled.

powder to a highly confined area. The sample tube and crucible were precision machined from Coors high-purity (99.5%) impervious Al_2O_3 in order to optimize volume ratios with these points in mind. Alumina was chosen as a sample container because our experience has been that surface reaction with rare earths or actinides occurs rapidly only near the sesquioxide composition and at temperatures $> 1200^\circ\text{C}$.

An uncalibrated thermocouple was used in all work reported for the BkO_2 and CeO_2 experiments. Calibration of three thermocouples from the same lot of wire used in these experiments, however, were identical with less than 2° correction at all temperatures. This is felt to be within limits of error, considering other problems of temperature measurement, and no corrections were applied to the measured temperatures. Temperatures were measured by a Pt/Pt-10% Rh thermocouple (0.008 in. diam) to 0.001 mv on a Rubicon potentiometer with an ice water junction reference. The thermocouple was within 1/8 in. of the sample and careful measurement of the furnace profile indicated agreement to $\pm 1^\circ\text{C}$ for temperatures at the sample and thermocouple positions. The small BkO_x sample occupied only 0.020 in. along the furnace axis. The 1/2" I.D. alumina furnace tube was wound with 0.040" Pt-40% Rh wire insulated with alumina wool and placed within a water cooled stainless steel shell.

A trace analysis of alumina from the same purchase lots as was used for the BkO_x sample tube system indicated >0.01 wt% Si, ~ 0.01 wt% ea. B, Fe, Mg, and <0.01 wt% Cr, Cu, Ga, Mn. The alumina crucible, sample tube, and filler rod were cleaned in aqua regia, ultrasonic cleaned in distilled water, and air fired to 1600°C before use. All gas used in the study was Matheson 99.95% purity.

The mass analysis of the berkelium by ORNL was made prior to the oxalate precipitation which further purified the sample. The analyses, which for the most part were at limits of detection, are given in weight %: Ta 0.015, total rare earths <0.02 , Ba 0.02, Zr 0.21, Fe 0.054, Cr 0.012, Ti 0.06, Ca 0.30, K 0.012, P 0.05, S 0.2, Si 0.3, Al 0.03, Mg 0.05, and Na 0.05.

The Bk^{249} isotope used in the experiments was synthesized in the High Flux Isotope Reactor at ORNL, where it was also separated and purified. The

final HCl solution was loaded into the Al_2O_3 crucible shown in Figure 4 and precipitated as the oxalate. Following a drying procedure, the sample was suspended from a Cahn thermobalance and heated to 1050°C both in air and pure oxygen. Final room temperature weighings on two microbalances agreed within 0.005 mg and the final weight as BkO_2 was 1.220 mg. The sample was shipped in our crucible with a solid cap in place of the slotted one.

The sample crucible arrived at BNW in a 2" x 2" polished stainless steel cylinder which had previously been sent to ORNL. The Al_2O_3 crucible rested within a larger Al_2O_3 crucible to prevent metal pickup and was held firmly in position by a spring loaded piston in the upper half of the cylinder. Thanks to careful handling at ORNL, the crucible and containing cylinder arrived free of external radioactive contamination. The alumina sample tube and filler rods were placed in a plutonium contaminated glove box which had been thoroughly washed prior to receiving the sample. This facility was also kept inactive for several weeks prior to the loading with a reduced inert gas flow to minimize dust movement. The sample tube was shielded from possible contamination by placement within a test tube with a 0.002" mylar film extending within the sample tube, protecting the lip area. The solid cap was removed from the sample containing crucible, replaced by the slotted cap, and slipped into the sample tube after which the filler rods were entered. The sample tube was separated from the outer protective test tube in an air lock and was successfully removed and sealed to the manometer system in an open front hood. No external radioactivity was encountered throughout these handling activities or during the course of the experiments.

Following the experiments, the sample tube was placed in the same glove box and the crucible removed from the tube assembly by cementing a rod to the cap and removing it in a horizontal position. The cap and crucible did not separate by this procedure, as anticipated, and the sample was thus returned without mishap to ORNL for reprocessing.

TRIAL RUNS

The system and technique were evaluated through several types of experiments both before and after the BkO_x study. The rare earth oxides served as good stand-ins in this respect and "isobaric" decompositions of PrO_x were successfully completed before the BkO_x runs. Experiments on CeO_x using a procedure identical to that used on BkO_x were completed after the BkO_x study. As a test of ultimate sensitivity, decomposition studies of 30 and 4 μg samples of CaCO_3 were carried out. Certain problems due to the Al_2O_3 system (or associated impurities) had some effect on the results and certain aspects of this problem are discussed below.

Problems inherent in the nature of such a micro-system have been alluded to. Temperature control is critical. In measuring pressure changes of <2 Torr as was done in these experiments, it is desirable to measure pressure to ± 0.001 Torr. For total system pressures approaching 1 atmosphere, this means temperature control to $\pm 0.001^\circ\text{C}$ would be desirable while at 10 Torr total pressure, control to $\pm 0.03^\circ\text{C}$ is sufficient. At very low pressures, outgassing problems become uncontrollable even though temperature control need be only minimal.

A consideration of the ideal gas law reveals that volume changes are no more tolerable than temperature changes. In the ΔP range employed in this study (1-10 Torr), the manometer diaphragm deflections of fractions of a micron result in essentially zero volume changes. It was necessary, however, to consider volume changes due to heating the sample tube and, as discussed later, this can be accurately accounted for.

With temperature and volume control maintained, the only other problems relate to sources of unanticipated pressure changes. These include possible sorption - desorption effects on walls of the system or sample, and a leak rate normally acceptable in much higher vacuum work is unacceptable in this type of system. After considerable effort, the desirable zero leak rate was achieved. Simple sorption - desorption type problems were of no consequence in the experiments on BkO_x as will be shown later. The evaluation experiments carried out are discussed under section (1) PrO_x (2) Al_2O_3 (3) CeO_x and (4) CaCO_3 .

1. PrO_x

The decomposition of a 1.0 ± 0.1 mg sample of $\text{PrO}_{1.800}$ was continuously monitored on a two-pen potentiometric recorder. The sample tube system consisted of a heavy walled quartz tube with ~ 1 mm I.D. and the crucible was fashioned from a $1/2$ in. length of alumina thermocouple sheathing. The results of two consecutive runs over a three-day period with both heating and cooling gave essentially identical curves as shown in Figure 6. The initial pressure of 9.30 Torr O_2 at 400°C rose to ~ 9.44 Torr at 800°C due both to decomposition and a P-T effect due to simple heating of part of the system. The data are, therefore, not strictly isobaric. The curves in Figures 6 are not corrected for the P-T effect and thus, the three "vertical" portions would be slightly more vertical after correction.

The data are in excellent agreement with the phase changes given by Hyde et.al,⁽⁶⁾ who performed thermogravimetric experiments using multigram samples. If the compositions of the end phases (Pr_5O_9 and Pr_7O_{12}) are chosen to be ideal at the point of intersection of the heating and cooling curves (admittedly arbitrary), a relation between ΔX and ΔP is fixed from which the composition of the intermediate phase can be calculated. The "calculated" stoichiometry of this phase is $\text{PrO}_{1.7773}$ which compares extremely well with the ideal value for Pr_9O_{16} of 1.7778. There is no doubt that this system is capable of stoichiometry measurements to better than ± 0.001 in. x for MO_x using 1 milligram samples. In terms of weight changes, this is equivalent to about ± 30 nanograms. In these experiments, pressure changes of 0.0001 Torr could be read from the chart paper giving a sensitivity approaching 20 nanograms in terms of mass.

Some experiments in hydrogen were carried out with the same PrO_x sample. Part of the reaction tube was maintained at -60°C by a methanol-dry ice bath. Thus, the reduction of the sample could be followed by a decreasing H_2 pressure according to the reaction:

Although some changes in rate of reaction were observed, a clear relation to the several stoichiometric phases was not obtained. The low temperature of reduction ($\lesssim 400^\circ\text{C}$) probably inhibits complete ordering necessary for the formation of intermediate phases and unless the reduction were carried out extremely slowly, simultaneous reduction of all phases would occur.

FIGURE 6. Oxidation-reduction cycle for 1.0 mg of PrO_x as a function of temperature at ~ 9.5 Torr O_2 .

This would be a difficult approach to phase studies in a system of this type and was abandoned.

It might be pointed out that reactions with H_2 are observed equally well as those with O_2 on a mole basis. In terms of weight change, the sensitivity is 16 times greater so that hydride equilibria for example, could be monitored with extremely high sensitivity compared to gravimetric methods.

2. Al_2O_3

The suspected high temperature stability of berkelium oxide required conversion of the system from quartz to alumina. Several flat bottomed tube assemblies were precision machined only to find an intolerable out-gassing effect at $T \gtrsim 1000^\circ C$. It was incorrectly concluded that the commercial alumina cement used to seal the bottom plug in these assemblies was the cause of the problems. A second set of round bottom tubes (closed one end as supplied) was made suitable by machining a plug to fill the bottom curvature (see Figure 4) which, however, gave identical results to the first tubes. Several possible causes i.e., thermal expansion effects, heat flow, etc., were considered and ruled out experimentally. As the number of observations increased, a general behavior pattern emerged which can be described by two of the experiments as shown in Figure 7. Run A is a heating - cooling curve for the system in 10 mm O_2 . The pre-treatment involved pumpdown of the entire system to 1×10^{-5} Torr at $800-900^\circ C$. Curve I is a heating - cooling run in ~ 3 Torr O_2 . The pre-treatment in this case, however, involved system pumpdown to 1×10^{-5} Torr at $\sim 1300^\circ C$ and cooling to room temperature under vacuum. In both runs, a normal P-T effect is observed initially. However for Run I, an abnormal plateau is reached at $\sim 500^\circ C$ and decreasing pressure is observed by $\sim 800^\circ C$. For Run A, pressure decreases at slightly higher temperature and is far less severe. In both cases, a temperature is reached at which the pressure starts rising rapidly. In one experiment, this rising pressure was observed to continue for five hours (at $\sim 1200^\circ C$) at a slightly decreasing rate versus time.

The phenomena appears to be diffusion controlled and the magnitude and longevity of the pressure changes rules out a surface effect. It is

FIGURE 7. Sorption effects in the alumina system at low O₂ pressures.

estimated that some 30-40 grams of Al_2O_3 are in the hot zone and in communication with the manometer. The dissociation pressures over pure Al_2O_3 are much lower than the observed anomalies, however, impurities of $\sim 0.01\%$ (40 mg) can have profound effects. If we consider dissociation pressures of the pure oxides that are present in trace quantities, those of Cr, Mn, and Cu are particularly suspect, but no quantitative analysis can be made since the behavior of these oxides in such dilute solution is unknown.

At higher oxygen pressures (>30 Torr), a more satisfactory behavior was observed. Thus, the curves at 50 and 250 Torr shown in Figure 8 show only moderate anomalies. Because the hot zone volume decreases with increasing temperature, a regular P-T curve with decreasing slope ($\Delta P/\Delta T$) should be obtained. Since this is observed only to $\sim 1100^\circ\text{C}$, it would seem that some species undergoes reduction even in 250 Torr O_2 , at or before this temperature. As will be discussed, these problems had some effect on both CeO_x and BkO_x experiments.

3. CeO_x

The CeO_x data are summarized in Table I. These measurements of stoichiometry vs $\log P_{\text{O}_2}$ were carried out on ~ 1 mg samples of CeO_2 in a manner identical to that followed for the BkO_x experiments. The ceria data obtained by Kordis⁽⁴⁾ differ from our data by a mean value of $+0.013$ in x , and a much higher scatter was observed for these experiments in comparison to the BkO_x work. A certain portion of the discrepancy and the increased scatter can be accounted for as related to several problems which become apparent as the CeO_x experiments proceeded.

It was observed that following a sample pre-treatment of heating to $\sim 900^\circ\text{C}$ and pumping to $\sim 1 \times 10^{-5}$ Torr in either alumina or Pt containers, a light-blue product was obtained. These samples could be converted to the usual cream-white CeO_2 by heating to $\sim 400^\circ\text{C}$ in air. This suggests, contrary to the known dissociation pressures, that a substoichiometric oxide was obtained. The CeO_2 used was the highest purity available (Lindsay 99.999% with respect to other rare earths) and no explanation is obvious. This blue-colored product

FIGURE 8. Sorption effects in the alumina system at high O_2 pressures.

TABLE I. CeO_x DataSample 1 1.209 mg CeO_2

Oxidation at 500°C

Run	ΔP_{O_x} (Torr)	O/Ce	Kordis* O/Ce	$\Delta(O/Ce)$	T(°C)	$\log p_{O_2}$ (atm.)
1	0.2438	1.9502	1.969	-0.019	872	-18.00
2	0.5462	1.8884	1.917	-0.029	971	-15.94
3a	0.2512	1.9487	1.969	-0.020	872	-18.00

Sample 1 Oxidation at 350°C

3b	0.1981	0.9595	1.969	-0.009	872	-18.00
4	0.4592	1.9061	1.917	-0.011	927	-15.94
5	0.6262	1.8720	1.880	-0.008	1079.5	-14.02
6	1.1573	1.7635	--	--	1100	H ₂
7	1.3404	1.7260	--	--	1200	H ₂
8	0.2087	1.9573	1.975	-0.018	747	-21.16
9	0.5107	1.8956	1.917	-0.021	971	-51.94

Sample 2 1.424 mg

Oxidation at 350°C

100	0.7717	1.8668	1.880	-0.013	1079.5	-14.02
101	0.2529	1.9564	1.969	-0.013	872	-18.00
102	1.1525	1.8011	1.775	+0.026	1079.5	-17.04
103	1.1611	1.7996	1.775	+0.025	1079.5	-17.04

*Ref 4

was also obtained as a result of oxidation in 7 Torr O_2 at $350^\circ C$. It is believed that this coloration is the result of some impurity stabilization of very slightly reduced CeO_2 , e.g., $CeO_{1.9995}$.

The second difficulty encountered with the CeO_x runs was that the oxidation, and gas expansions into the sample tube without oxidation (to a lesser extent), resulted in a long-term drift which was not negligible even after several hours at $500^\circ C$. At $350^\circ C$, the continuing O_2 uptake was negligible after one-half hour ($<1 \mu/10 \text{ min.}$). This same problem was observed for the BkO_x runs only for oxidations following H_2 reductions and to a less severe extent. (For BkO_x runs, the pressure leveled at $500^\circ C$ in a few minutes for normal oxidations and relative volume determinations.) Relative volume expansions using argon, with the CeO_2 sample in place, gave pressure plateaus almost immediately. With the sample removed, there appeared to be little or no change in this drift problem so it was perhaps only good fortune that the alumina sample tube containing the BkO_x sample was better behaved.

Two types of repetitive gas expansions were carried out during the course of the work. In the oxidation type expansion, the measured ΔP was due to oxidation of the sub-stoichiometric sample and simple gas expansion. In relative volume expansions the sample was already fully oxidized. The expansion of gas from within the thermostated box into the sample tube, gave two pressures, P_b and P_c associated with the internal volume V_b and total volume V_c . In the case where oxidation also occurs, the latter pressure is, in the following discussion, denoted as P_c . There was the possibility that in addition to these contributions to a measured ΔP , that system problems already discussed would have some effect. Two blank runs were carried out with the CeO_2 sample tube assembly (no sample) using the gas mix $CO_2/CO = 0.223$. A procedure identical to that used for the BkO_x and CeO_x run was followed at $852^\circ C$ and $1150^\circ C$. The "oxidation" following these equilibrations gave nearly identical P_b/P_c values to the relative volume expansion at $350^\circ C$:

$$P_b/P_c = 1.1738 (852), 1.1735 (1150), 1.1735 (\text{rel. vol.})$$

These blank runs demonstrate a negligible CO_2/CO effect but do not rule out the possibility of a necessary correction due to the drift effect as discussed later. We believe that this drift effect is related to the Al_2O_3 problems previously discussed and that at $350^\circ C$, the diffusion of O_2 back into the system is slow and incomplete.

If it is assumed that the CeO_2 composition is achieved immediately and the observed O_2 pickup after $t \approx 0$ is due only to the system, then system sorption following oxidation was ~ 0.03 Torr compared to ≤ 0.01 Torr following relative volume expansions. Oxidations following H_2 reductions

gave much larger sorption effects of ~ 0.1 Torr. In a small way, this mirrors the history dependence described earlier since the magnitude of the sorption effect relates to the reducing potential set by these three operations in the order - relative volumes < oxidations < H_2 reduction.

The differences between the CeO_x data from these experiments and Kordis⁽⁴⁾ results can be explained by a system sorption of ~ 0.06 Torr. The observed value of ~ 0.03 Torr could conceivably be larger since pressure is changing rapidly near $t = 0$ and the graphical extrapolation may not be drawn steeply enough.

It should be pointed out that the last two ceria runs (Runs 102 and 103 in Table I) with $CO_2/CO = 0.0071$ and $T = 1079^\circ C$ gave an apparent stoichiometry difference of 0.026 in O/Ce higher than Kordis' data. As will be shown by the BkO_x data, the partial oxygen pressure calculated by this CO_2/CO ratio was not obtained. The true pressure was higher and determined by the temperature of the system. Thus, an apparent high stoichiometry was measured. Contrary to the experience of others in using a flow of dry hydrogen, it was not possible to fully reduce CeO_x in our closed system. On heating CeO_2 in hydrogen at $1100^\circ C$ and $1200^\circ C$, O/Ce values of 1.763 and 1.726, respectively were obtained. Based on the results of Kordis⁽⁴⁾ the oxygen pressure in equilibrium with these compositions at $1100^\circ C$ and $1200^\circ C$ is $\log P_{O_2} = -16.8$ and $\log P_{O_2} = -15.4$, respectively.

From the BkO_x data, it can likewise be shown that hydrogen reduction at $850^\circ C$ resulted in $\log P_{O_2} = -19.5$. These points, plotted in Figure 9, give a qualitative picture of the limiting O_2 pressures in the system employed. It is suggested that reduction of impurities within the Al_2O_3 limits the partial oxygen pressure attainable within the system.

FIGURE 9. Limiting O_2 partial pressures in the alumina system in a static hydrogen atmosphere as a function of temperature.

Because the difficulties observed during the CeO_x runs were at least an order of magnitude greater than the BkO_x runs, and because the differences between our results and those of Kordis on CeO_x are relatively small, no attempt has been made to apply any corrections to the BkO_x data.

4. CaCO_3

Several experiments were carried out on microgram samples of CaCO_3 in order to test the ultimate sensitivity of the system. The first attempt using the all alumina tube assembly used for the CeO_x runs was unsuccessful due to large outgassing effects. Subsequent experiments with a quartz sample tube of ~ 1 mm I.D. and an alumina crucible fashioned from thermocouple sheathing were satisfactory. These experiments were carried out using 1.5 ± 2 μg (actually 3.77 μg) CaCO_3 at a heating rate of $2^\circ\text{C}/\text{min}$. and 30 ± 2 μg CaCO_3 at a heating rate of $10^\circ\text{C}/\text{min}$. Pretreatment on the 30 μg sample consisted of pumpdown to $< 1 \times 10^{-5}$ Torr with the sample temperature at 150°C for ~ 2 hours. The experiment with the smaller sample consisted of a similar pumpdown at 150°C but for 15 hours. Both the quartz tube and crucible were torched to a red heat within an hour of final sealing to the system.

A reproduction of the actual recorder trace for the smaller sample decomposition is shown in Figure 10. This is, to the best of our knowledge, the smallest sample of any material for which accurate and continuous monitoring of thermal decomposition has been made. This decomposition was observed to proceed over > 5 widths of 10 in. chart paper. The quantity of gas

FIGURE 10. Actual recorder trace for the thermal decomposition of 3.77 μ g sample of CaCO₂ at a heating rate of 2°C/min.

being measured may be evaluated through the ideal gas law resulting in $\Delta n = 3.77 \times 10^{-8}$ moles or 3.77 μg of CaCO_3 were initially present. With 100 ruled divisions per chart width and estimates to 0.1 of a division possible, a sensitivity of $\sim 5 \times 10^{-11}$ moles CO_2 was achieved in this experiment. In terms of mass, this is $\sim 2 \times 10^{-9}$ grams. We believe the system is capable of an accuracy to at least $\pm 5 \times 10^{-10}$ moles of gas which represents an improvement of $\sim 10^3$ over conventional thermobalance techniques.

With the 30 μg sample of CaCO_3 the net ΔP due to decomposition was 0.3821 Torr. This gives a calculated sample weight of 27.88 μg as CaCO_3 , which agrees well with the pre-measured sample weight of $30 \pm 2 \mu\text{g}$.

In Figure 10, the increasing slope observed at the CaCO_3 and CaO phases is due to outgassing for the former and a combination of outgassing and a P-T effect for the latter. For precise data, the outgassing and P-T effects must be subtracted from the observed curves.

The latter correction is not difficult in practice, although every pressure requires a different correction. The former effect has been found to be nearly linear over short time or temperature spans and over short temperature ranges. For sufficiently small hot zone volumes, the P-T effect is also linear. Hence, the pressure changes observed with linear temperature change (vs. time) for the CaCO_3 and CaO phases were very nearly linear. Corrections to be made in the transitory region are nonlinear, but can be made relatively accurately by graphical means. Exact corrections can be made easily by computer methods for detailed or repetitive investigations. A graphical method was used to give the corrected curves shown in Figure 11.

FIGURE 11. Corrected pyrolysis curves for 3.77 μg and 27.88 μg samples of CaCO₃.

It was not the intent of these experiments to add to the already copious data available on pyrolysis of CaCO_3 . The observed temperatures for initial and final decompositions are within (on the low side) of those reported for multi-milligram samples. The observed temperature span for start and finish of decomposition is much smaller than reported for large samples even at slower heating rates. Thus, Richer and Vallet⁽¹⁸⁾ give $\Delta T = 183^\circ\text{C}$ for a 250 mg sample at a heating rate of 19°C/hr and $\Delta T = 215^\circ\text{C}$ at 100°C/hr . We obtained $\Delta T = 71^\circ\text{C}$ at 120°C/hr and $\Delta T = 103^\circ\text{C}$ at 600°C/hr for the 3.77 μg and 27.88 μg samples, respectively.

Some general comments concerning the use of such a system in solid state investigations should be made. More quantitative analysis of errors are made following the BkO_x results, but it may be stated here that the extreme sensitivity already demonstrated is coupled to a high degree of accuracy. In addition to the types of experiments discussed, such properties as surface area, density, volume changes (with melting for example), surface phenomena (physical and chemical adsorption), kinetics of reaction or decomposition, etc., can all be performed with only minor modifications in sample containment. The choice of materials must be carefully considered. Quartz is an ideal material because of its very low thermal expansion coefficient and its ease of outgassing, but materials and ultimate design as in any experiment need to be tailor fit.

In general, this technique is most powerful in experiments which monitor gas - solid equilibria and the system shown in Appendix A is particularly well suited for this type of study. During completion of this work, a paper was published⁽¹⁹⁾ in which slight deviations in stoichiometry

were measured on ~10 g samples as a function of pressure in Co_2SiO_4 and in CoAl_2O_4 - MgAl_2O_4 . The apparatus⁽²⁰⁾ used is identical in concept to that described in Appendix A. It was, however, constructed of glass, employed a less sensitive capacitance manometer, was not thermostated, and was not micro-scale volumetrically. Their apparatus was accurate to 10^{-7} moles of evolved gas which is several orders of magnitude less sensitive than the system described here. No discussion of errors was given in the paper, although it is mentioned that irregularly shaped curves due to thermal fluctuations and adsorption effects are sometimes obtained above 80 Torr with quartz sample tubes.

BkO_x PROCEDURES

1. Experimental

The actual "recipe" followed in order to obtain one (P, T, X) data point in the BkO_x study is given in Appendix B. If no difficulties were encountered (such as poor pumping efficiency) an average of one point per five hours was obtained. Data were taken by three individuals on an around-the-clock effort, all following this procedure quite closely. It was determined that a pressure of 1×10^{-5} Torr, as measured in close proximity to the diffusion pump, corresponded to a true pressure of 10^{-3} - 10^{-2} Torr at the end of the sample tube. This is the point farthest removed from the pump and the large pressure gradient is due to the small diameter tubing (used to minimize system volume) and a tortuous pumping path. The volume outside of valve X2 (see Figure 3) was 17% of the total V_x volume.

Thus, assuming a worst case vacuum of 5×10^{-3} Torr for this 17%, a ΔP error of ~ 0.0006 Torr would result. In terms of O/Bk, this is ~ 0.0005 , which is negligible.

2. Data Reduction

There are two main approaches available in treating data obtained on a metal-oxygen system:

- A. Through the ideal gas law assuming
 - (1) an O/M ratio for a known weight
 - (2) a known ratio (V/T) for the system.
- B. Empirically through an assumption of two oxidation states (in this case $MO_{1.50}$ and $MO_{2.00}$) for which the oxidation $MO_{1.50} \rightarrow MO_{2.00}$ gives a system "calibration," i.e., $(\Delta X/\Delta P)_O$. Measurement of ΔP on subsequent oxidations from an unknown composition $MO_x \rightarrow MO_{2.00}$ then immediately gives x with no further assumptions. Other possible variables need be maintained constant (but not known).

It is clear for reason of simplicity that approach (B) would be more desirable. A comparison of results obtained using both approaches indicated, however, that either the sample weight supplied by ORNL was high by ~ 0.1 mg or that the assumed stoichiometry $MO_{1.500}$ was incorrect. Based on the information generated by the CeO_x experiments it is known that the hydrogen reductions carried out did not generate the calculated low O_2 partial pressures. As will be later shown, the BkO_x data in themselves show, that at higher temperatures the low partial pressures supposedly determined by the CO_2/CO ratio, were not obtained.

The results of the hydrogen reduction and subsequent oxidation experiments carried out on BkO_x are summarized in Table II. The mean ΔP_{O} of 1.366 Torr may be compared to the value calculated according to approach (1) of 1.5105 Torr. Using the former value, it is seen that $\Delta X = 1.366 \times 0.1/1.5105 = 0.451$. The hydrogen reductions thus resulted in a mean composition of $\text{BkO}_{1.549}$. Consideration of the dissociation pressure data discussed previously indicates that with hydrogen in the system at 850°C , a true partial oxygen pressure was obtained such that $\log P_{\text{O}_2} \sim -19.5$ at 850°C .

For this reason the more simple empirical approach could not be used in interpreting the data. The analysis through the ideal gas law required an accurate determination of the volume/temperature ratio. The experimental details of this determination and the data reduction are discussed below.

a. General

The oxygen/metal ratio of a given sample was determined following equilibration with a known CO_2/CO ratio at each of five temperatures. The free energy equation given by Kubaschewski and Evans⁽²¹⁾ was used to evaluate oxygen partial pressures according to:

$$\Delta G^\circ = -RT \ln K = -67,500 + 20.75T$$

TABLE II. H_2 Reduction, Oxidation Runs

<u>Run #</u>	<u>Days</u>	<u>ΔP_i</u>	<u>ΔP_o</u>	<u>T°C(of reduction)</u>
33a	22.0	1.335	1.402	750
33b	22.1	1.339	1.406	800
59	27.9	1.309	1.392	900
111	38.0	1.247	1.356	850
112	38.1	1.244	1.353	850
118	39.1	1.234	1.346	850
133	51.3	1.226	1.394	750
134	51.5	1.210	1.356	850
136	52.5	1.209	1.358	850
137	53.3	1.216	1.368	850
138	56.2	1.191	1.348	850
139	56.5	1.192	1.350	850
140	56.8	1.197	1.357	850
141	57.2	1.194	1.355	850
142	57.5	1.192	1.353	850
143	57.7	1.214	1.379	750

Mean $\Delta P_o = 1.366 \pm 0.02$ Torr.

or

$$\log P_{O_2} = \frac{-29,508}{T} + 2 \log \frac{P_{CO_2}}{P_{CO}} + 9.071$$

The CO₂/CO mixtures were prepared by use of a cathetometer and mercury manometer to fill four 5 liter storage bulbs. A number of the mixtures were analyzed on a mass spectrometer for which satisfactory agreement (considering the low spectrometer sensitivity) was obtained as shown in Table III.

The stoichiometry of reduced oxides was determined by oxidation of the samples at 500°C. This choice of oxidation temperature was made since this was the highest temperature at which the anomalous system behavior described previously could be considered negligible. It would obviously be most desirable to carry out oxidations at the temperature of CO₂/CO equilibration since the time expended per data point would be ~1 hour instead of 5 hours.

After equilibration of the sample with the desired CO₂/CO gas, the sample tube was evacuated and isolated from the manometer. The oxygen pressure was then set at ~7.4 Torr, read exactly on the manometer, and the gas then admitted to the sample. The pressure which should result if only gas expansion occurred was determined from a large number of such relative volume expansions carried out when the O/Bk was known to be 2.000. The initial pressure P_b divided by this ratio $(P_b/P_c)_0 = 1.1755$ gave the expanded gas pressure P_c which could be compared to the measured pressure P'_c . The difference between these two is a direct measure of the oxygen involved in oxidation of the nonstoichiometric oxide to BkO_{2.000}.

Through the ideal gas law the relation between stoichiometry change and ΔP_{Ox} can be determined.

Consider:

At constant V and T,

TABLE III. Gas Analyses

<u>Runs</u>	<u>CO₂/CO Ratio</u>	
	<u>Measured</u>	<u>Mass Spec.</u>
20-22	0.336	0.34
23-25	0.099	0.11
26-32	0.985	1.04
34-36	7.985	8.16
41-46	2.174	2.04
121-122	94.615	~1000
123-124	37.94	41.30
125-126	15.172	15.62
130, 132, 140	0.0331	0.02
145-147	1002.8	~ ∞
CeO ₂	0.223	0.22
CeO _x	0.007	0.008

$$\Delta PV = \Delta nRT$$

$$\Delta n = 1/4 (W_{\text{BkO}_2} / ATW_{\text{BkO}_2})$$

$$\Delta P_o \text{ (Torr)} = 15.590 \left(\frac{W}{ATW} \right) \left(\frac{T}{V} \right)$$

w in mg., T in °K, V in ml.

for BkO_2 $W = 1.22$, $ATW = 281$

$$\left(\frac{\Delta X}{\Delta P_o} \right) = 0.5/15.590 \left(\frac{1.22}{281} \right) \left(\frac{T}{V} \right)$$

Then neglecting radioactive decay of the sample, the stoichiometry of a given preparation, i , is given by

$$X_i = 2.000 - \Delta P_i \left(\frac{\Delta X}{\Delta P_o} \right)$$

b. Volume

Preceding the experiments, a glass bulb of known volume was connected to the system via small bore tubing. The volume of the bulb was determined by a comparison of the weight when evacuated ($\sim 30\mu$ Torr) and filled with mercury. The mercury temperature was measured with an N. B. S. calibrated thermometer to 0.01°C and published density data⁽²²⁾ was used. The mean of six determinations was $33.706 \pm 0.002 \text{ cm}^3$.

The total system including this known volume (on the external glass rack), connecting tubing, the sample side of the manometer, and all connecting valves may be represented schematically:

where V_R is the known reference volume and V_x is the volume to be determined. Room temperature was monitored during the volume determination and fluctuated within 0.5°C of 24.8°C over the period of measurements. The furnace temperature was 500°C which complicates an absolute volume measurement, but the following expressions are seen to hold:

$$\frac{P_1 (V_x)}{T_E} = P_2 \frac{(V_x + V_v + V_T + V_S + V_R)}{T'_E}$$

$$\frac{P_3 (V_R)}{T''_E} = P_4 \frac{(V_x + V_v + V_T + V_S + V_R)}{T'_E}$$

$$V_x = \left(\frac{P_2}{P_1}\right) \left(\frac{P_3}{P_4}\right) \left(\frac{T_E}{T''_E}\right) V_R$$

Here T_E is an effective temperature to which the entire volume (V_x) would have to be raised to give an effect equal to that obtained by heating the sample tube to 500°C and T is the reference volume temperature which was $298.0 \pm 0.2^\circ\text{K}$. As previously given, $V_R = 33.706$ cc. The mean of 5 determinations each was:

$$(P_2/P_1) = 0.04184 \pm 2$$

$$(P_3/P_4) = 9.507 \pm 4$$

Then:

$$V_x = 0.04184 \times 9.507 \times 33.706 \frac{T_E}{298}$$

$$V_x = 13.407 \frac{T_E}{298} \text{ cc.}$$

Although T_E can be estimated and an absolute volume obtained, this was not necessary as shown below.

c. Temperature

In making calculations through the ideal gas law, the temperature must be specified. In the BkO_x oxidations, this temperature has been defined as T_E .

and is slightly larger than 298.0 K. From section (a), the expression through which stoichiometry is calculated is:

$$X_i = 2.000 - \Delta P_i \left(\frac{\Delta X}{\Delta P} \right)_0$$

where

$$\left(\frac{\Delta X}{\Delta P} \right)_0 = 0.5 / \left[15.590 \left(\frac{1.22}{281} \right) \left(\frac{T_E}{V_x} \right) \right]$$

and previously it was shown that

$$V_x = 13.407 \left(\frac{T_E}{298.0} \right)$$

which gives

$$\left(\frac{\Delta X}{\Delta P} \right)_0 = 0.5 \left[15.590 \left(\frac{1.22}{281} \right) \left(\frac{298.0}{13.407} \right) \right]$$

$$\left(\frac{\Delta X}{\Delta P} \right)_0 = 0.33234$$

Thus it is not necessary to know either the effective temperature, T_E or the absolute system volume, V_x , but only their ratio.

d. Decay Corrections and Final Equations

At the time of the BkO_x work there was no evidence that Cf^{+4} could be formed. However, there have recently been two compounds prepared with Cf in the +4 state.⁽¹⁷⁾ It appears that under the conditions of the BkO_x experiments, Cf remained in the +3 state and the following derivations are made under this assumption. It is moreover assumed on the basis of the known existence of the isostructural sesquioxide of Bk and Cf and their nearly identical radii, that complete solid solutions are formed over the range of [Cf] encountered in these experiments. For the 314 day half-life for decay, the decay constant

$$k = -\ln(0.5)/314$$

The ternary at any time may be expressed as

where $z = 1/2$ the mean Bk oxidation state

and $y = [Cf]/([Cf] + [Bk])$

or $y = (1 - e^{-kt})$

Since only Bk undergoes oxidation, the O/Bk ratio (i.e., z as defined above) is determined experimentally. Then as above, but considering the time dependence:

$$O/Bk = 2 - \Delta P(\Delta X/\Delta P)_t$$

$$O/Bk = 2 - \Delta P(0.5/\Delta P_0 e^{-kt}) = z$$

where ΔP_0 refers to $[Bk] = [Bk]_0$

In reality, it would seem that one should consider O/(Bk, Cf) ratios since the homogeneous introduction of Cf by the beta decay results in a true ternary system. Referring back to the formula of this ternary it is seen that:

$$\begin{aligned} O/(Bk, Cf) &= [1.5 y + z(1-y)] / [(1-y) + y] \\ &= z(1-y) + 1.5 y \end{aligned}$$

or

$$O/(Bk, Cf) = 1.5 + 0.5 e^{-kt} - \Delta P(0.5/\Delta P_0)$$

The data to be discussed were thus also analyzed through this equation which apriori would seem to be the best approach. It will be noted that in both cases (binary and ternary), it has been assumed that the change in O/Bk for the case $[Bk] = [Bk]_0$ is 0.500 in going from the fully reduced to fully oxidized state. Actually, whether this is true in reality is not relevant. It is important that the O/Bk ratio be 2.000 at 500°C and ~6 Torr O_2 (oxidation conditions). The data support this assumption from a dissociation pressure standpoint - i.e., a maximum oxidation state should be reached under these conditions. The light colored product observed when the sample was removed suggests that this composition was attained since even slight nonstoichiometry in these systems generally gives a dark product.

e. Partial Thermodynamic Quantities.

As will be discussed later, the data are considered isothermally with stoichiometry as one axis and some function of oxygen pressure the other. The isotherms so plotted consist of bivariant regions representing a single nonstoichiometric condensed phase and univariant plateaus representing a diphasic condensed region. The thermodynamic analysis may be performed using the following relations:

$$\Delta\bar{G}(O_2) = RT \ln p_{O_2} = \Delta\bar{H}(O_2) - T\Delta\bar{S}(O_2) \quad (1)$$

$$\Delta\bar{S}(O_2) = -\partial\Delta\bar{G}(O_2)/\partial T \quad (2)$$

$$\Delta\bar{H}(O_2) = \partial(\Delta\bar{G}/T)/\partial(1/T) = \partial(R \ln p_{O_2})/\partial(1/T) \quad (3)$$

In practice, the usual approach is to plot, for constant compositions, either $\Delta\bar{G}$ vs T from which the slope is $-\Delta\bar{S}$ or $(R \ln p_{O_2})$ vs $(1/T)$ from which the slope is $\Delta\bar{H}$ and then calculate the complimentary function through equation (1). In the single phase nonstoichiometric fields, the data so determined represent heats of solution of one mole of oxygen in the compound of specified composition. The equilibria is:

where the quantity of the condensed phase is large enough that δ has negligible effect on the composition. In the diphasic fields, a heat (or entropy) of reaction is obtained where the equilibria is:

where (A) and (B) are structurally distinguishable phases and γ is not necessarily small.

BkO_x Results and Discussion

The numerical results of the study are fully tabulated in Appendix C in terms of stoichiometry, temperature, and oxygen partial pressure and the derived thermodynamic data are given as a function of stoichiometry.

Several of the experiments were made under identical conditions of pressure and temperature in which the equilibrium stoichiometry was approached from both higher and lower oxidation states. These agreed within 0.002 in x , indicating that equilibrium was achieved. Kinetically, the procedure of 5-fifteen minute flushes with >500 Torr of the CO_2/CO gas mix, was approximately a factor of ten greater than necessary, as shown by the data of Table IV for $\text{CO}_2/\text{CO} = 1.0$. Thus, a reduction in total CO_2/CO pressure to 1/3 of that normally used and a reduction in time of equilibration to 2/15 of the normal time, caused no change in the resulting stoichiometry at 850°C. As shown, a measurable effect was observed at 650°C.

TABLE IV. RESULTS OF KINETIC EXPERIMENTS

Run	T(°C)	Total P (torr)	Time(min.)/flush	O/Bk
(Fig. 12)	852	>500	15	1.720
154	852	660	2	1.719
155	852	187	2	1.722
156	650	174	15	1.725
157	650	179	2	1.830
158	650	175	8	1.740

The results of the experiments are given in Figure 12 as $\log P_{\text{O}_2}$ vs O/Bk. As has been previously discussed, these cover a range of continuously increasing Cf concentration which are indicated in the figure by changes in symbolism at 3, 6, and 10% californium concentrations. A main point to be noted is that the 1075°C and 1150°C isotherms are considered least significant due to external effects influenced by the alumina at these temperatures and that the thermodynamic treatment to be discussed was made only from the three low temperature isotherms.

In Figure 13 we show the data plotted as $\log P_{\text{O}_2}$ vs O/(Bk, Cf). There is a marked time dependence in contrast to Figure 12 which is a plot of $\log P_{\text{O}_2}$ vs O/Bk. It will be noted that the O/Bk plot essentially ignores the contribution of oxygen to the system by the presence of Cf_2O_3 . It assumes that

FIGURE 12. Equilibrium oxygen decomposition pressure isotherms for nonstoichiometric berkelium oxide plotted versus O/Bk. Temperature in °C.

this ingrowing species behaves essentially as an inert diluant. By the plot shown in Figure 13 we consider the $\text{Cf}_2\text{O}_3 \cdot \text{BkO}_x$ solid solution as though the oxygen associated with Cf^{+3} were equally available to the berkelium ions. As shown by the time dependency, this is not the case and the dissociation pressures over the ternary (at these temperatures) are nearly independent of $[\text{Cf}]$.

The plot of Figure 12 assumes that californium is present only in the +3 state. In view of the recent preparation of CfO_2 , which requires 100 atm O_2 ⁽²³⁾, the possibility that Cf exists at some higher oxidation state must be considered. It has been shown that heating Cf_2O_3 in air may result in slight oxidation⁽¹⁴⁾ above the sesquioxide. The conditions during this work involving ~6 Torr O_2 and 500°C should not be sufficient for oxidation of significant extent. If a higher oxidation state was somehow achieved, the data as plotted in Figure 12 would shift to higher O/Bk values than shown, in proportion to the californium concentration. By comparison with the ternary systems to be discussed, such an increased shift would be anomalous since these systems show little or no change in dissociation pressure with the first 15% dilution. We take as further evidence that Cf was in the +3 state, the light colored sample observed at the conclusion of the experiments.

In Figure 14, the free energy isotherms are plotted as a function of composition. The 1075 and 1150°C curves for O/Bk < 1.75 are here more clearly seen to be anomalous. At O/Bk < 1.60, the data at all temperatures appear to merge into a single curve which is again thought to be related to system effects. Isoplethal cuts of the $\log P_{\text{O}_2}$ data are plotted against $1/T$ in Figure 15. The 1075 and 1150°C points are displaced to a greater extent at lower O_2 partial pressures and the effect is greater at the higher temperatures. Although the fit is satisfactory at the higher compositions (at 1075 and 1150°C), none of these data were used in the thermodynamic treatment. At O/Bk > 1.80, we have used only the lower three isotherms to demonstrate the effect of the plateau at O/Bk = 1.917. A treatment of the data in which the plateau was not drawn (the isotherms were each fit to a quadratic curve), using all of the data gives heat and entropy curves not grossly different than reported.

FIGURE 13. Oxygen decomposition pressure isotherms plotted versus oxygen to total metal ratio. Temperature in °C.

FIGURE 14. Partial molar free energy per mole of O_2 versus stoichiometry in the BkO_x system.

FIGURE 15. $\log p_{O_2}$ versus reciprocal temperature at constant composition for BkO_x .

The slopes of the lines in Figure 15 give the enthalpy of solution (or reaction in 2-phase regions) and the entropy was calculated through the relation:

$$\Delta \bar{S} (O_2) = [\Delta \bar{G}(O_2) - \Delta \bar{H}(O_2)]/T$$

These derived data are shown in Figure 16 as a function of composition. We have used the 925°C data in constructing these curves near the diphasic boundaries since for the ($\alpha + \sigma$) region, the compositions of the boundaries are temperature dependent. The real construction is not easily arrived at since the derivation of the thermodynamic data relies on a temperature independence.

The decomposition pressure isotherms and related thermodynamic quantities, together with a knowledge of the behavior of similar mixed-cation oxide systems, allow inferences concerning the nature of the phase relationships in the condensed $BkO_2 - Bk_2O_3$ system. Positive identification of the phases in this system must, of course, await x-ray diffraction analysis.

In general, bivariant regions of the isotherms in Figure 12 are interpreted as indicating single nonstoichiometric phases, while the univariant plateau regions imply a diphasic condition in the solid. In accordance with rare earth oxide terminology, the broad low composition bivariant field (Figure 12) is designated σ , while that above the central plateau is termed α . The σ phase is believed to be related to the cubic form of the sesquioxide (bixbyite structure) which may be described as a supercell of eight fluorite (MO_2) cells. At the stoichiometric composition, the idealized structure contains 25% anion vacancies and can accommodate excess oxygen to form a nonstoichiometric phase over a broad composition interval. The σ phase differs from the fluorite (MO_2) parent by the creation of anion vacancies in a random fashion (i.e., random relative to long-range order though short range order cannot be ruled out). Evidence for the existence of these two phases (σ and α) has been reported for the majority of the fluorite related oxide systems over various ranges of stoichiometry.

The effect of californium on the magnitude of the dissociation pressures has been discussed. In other fluorite related ternary systems, slight displacements in the pressure-composition isotherms have been noted with the addition of a M^{+3} or M^{+5} ion, though generally this has been observed at higher concentrations of the additive ion than reached in this work (13% Cf). It was

FIGURE 16. Derived partial molar enthalpy and entropy for berkelium oxides. Cerium oxide data from Reference (5).

recently shown⁽²⁴⁾ in the $U_{1-z}Ce_zO_{2-x}$ system that at constant temperature and O_2 pressure, the change is to higher O/Ce with increasing U^{+4} concentration. For the $U_yTh_{1-y}O_{2+x}$,⁽²⁵⁾ the change is to lower O/U with increasing Th^{+4} concentration. Similar small shifts occur in the $(U, Pu)O_{2-x}$ system as discussed by Roberts and Markin.⁽²⁶⁾ The latter work also demonstrates a correlation between enthalpy changes and the defect structure in $U_yTh_{1-y}O_{2+x}$ as the Th^{+4} concentration varies. The structural detail necessary for such a correlation is not available for any of the other lanthanide or actinide oxide systems.

The interpretation of the plateau regions shown in Figure 12 is complicated by a variety of possibilities brought to light by very recent investigations of related systems. Of the pure actinide and lanthanide systems, PrO_x is the richest in terms of numbers of intermediate phases. In addition to α and σ type regions which probably occur in all binary fluorite related systems, ordered phases of relatively narrow width occur at $O/Pr = 1.71, 1.80, 1.82, 1.83$ ⁽⁶⁾. Some of these phases have been identified or indicated in the CeO_x ,⁽⁵⁾ TbO_x ,⁽⁷⁾ and CmO_x ⁽²⁾ systems.

In the mixed oxide systems, some similarities exist between the $(U,Ce)O_{2-x}$ system and the results obtained for berkelium oxides. A detailed x-ray study⁽²⁷⁾ of hypostoichiometric uranium - cerium oxides shows two fcc phases in equilibrium in the region $1.90 < (O/M) < 2.00$, which is the same interval in which a diphasic region was postulated for BkO_x . Further, the compositional width of this diphasic field (for $U_{0.25}Ce_{0.75}O_{2-x}$) decreases with increasing temperature and extrapolation shows possible closure of this field at about $1000^\circ C$ and $O/M \approx 1.96$. The CeO_x system is somewhat similar⁽⁵⁾ in that diphasic equilibria with a parabolic closure by about $685^\circ C$ occurs. At $650^\circ C$, the equilibrium compositions are $CeO_{1.95}$ and $CeO_{1.89}$.

A summary of pertinent work on mixed oxides of formula $HfO_2-M_2O_3$ and $ZrO_2-M_2O_3$ (where $M = Sc, Y$, or lanthanide cation) is given by Didot, Vicat and Deportes⁽²⁸⁾ and by Thornber, Bevan and Summerville⁽²⁹⁾ on the $ZrO_2-M_2O_3$ systems.

The $ZrO_2-Sc_2O_3$ system⁽²⁹⁾ and the $HfO_2-Sc_2O_3$ system⁽³⁰⁾ are remarkably different. At high temperatures, both of these systems show a number of broad nonstoichiometric regions extending over rather wide ranges of composition.

However, in the $(\text{Hf}, \text{Sc})\text{O}_x$ system at 1000°C , one fluorite and two rhombohedral structured phases exist in the close interval $1.90 < \text{O/M} < 1.94$, while in the $(\text{Zr}, \text{Sc})\text{O}_x$ system in the same region, tetragonal and fluorite related phases are found. Further, the 1.714 phase which is the most stable intermediate phase in the pure Ce, Pr, Tb, and Cm oxide systems appears in the $(\text{Zr}, \text{Sc})\text{O}_x$ system but not in the $(\text{Hf}, \text{Sc})\text{O}_x$ system. If we consider $\text{ZrO}_2\text{-M}_2\text{O}_3$ systems for $\text{M} = \text{La, Ce, Nd, Sm, and Gd}$, the 1.714 phase is not formed and a cubic pyrochlore intermediate of mean composition $\text{MO}_{1.833}$ is a predominant feature in the phase diagrams⁽³¹⁾ The latter systems have not been thoroughly studied below 1000°C so that structure at $\text{O/M} \sim 1.92$ cannot be ruled out. It has been shown that pyrochlore formation in these systems is dependent on cation radius ratios.⁽³²⁾ It may be noted that the idealized structure may be constructed of fluorite cells from which oxygen ions have been removed across body diagonals, the mechanism by which several of the other fluorite related intermediate phases can also be constructed.⁽³³⁾

It is clear that with the exception of the Ce, Pr, Tb, and Cm oxide systems, the other binary actinide oxide systems such as those based on U, Pu, Am, and Bk, and all fluorite related ternary systems, are each unique and often considerably different. There is no one system which can be compared directly to the BkO_x system. Three broad nonstoichiometric phases have been defined by the data and are designated σ, α' , and α as shown in Figure 17.

The nature of the phases within the univariant fields is not clear. The evidence of structure at $\text{O/Bk} \sim 1.92$ is likely related to similar structure in the $(\text{U}, \text{Ce})\text{O}_x$, $(\text{Zr}, \text{Sc})\text{O}_x$, $(\text{Hf}, \text{Sc})\text{O}_x$, and $(\text{Hf}, \text{Y})\text{O}_x$ systems. The diphasic region at $\text{O/Bk} \sim 1.79$ may include structure in terms of either pyrochlore or 1.800 phases (rhombohedral structure) or may be a simple two phase region of $\alpha + \sigma$. Precise clarification of phase relations in this system must await a determination of the effects of Cf ingrowth, i.e., during the first few percent of decay, and careful x-ray diffraction analysis. It should be further emphasized that although the presence of 2-13% Cf had little effect on the thermodynamic quantities within the α and σ fields as discussed earlier, the compositions near the diphasic plateaus were examined over relatively short

FIGURE 17. Composition of phase boundaries at 925°C

time periods and may well shift as a function of Cf concentration. If highly ordered phases of narrow composition width are formed at O/Bk $\sim$ 1.92, (or any other composition), the californium content must play an important role and oxygen/total metal ratios must be considered.

Error Analysis

The principal sources of experimental error deal with temperature measurement, knowledge of the CO/CO₂ ratio, and pressure measurement during oxidation to BkO₂. Based on the thermocouple calibration as well as potential errors in the measuring circuit, the uncertainty in the temperature is estimated to be $\pm 3^\circ\text{C}$. Comparison of the CO/CO₂ ratios measured cathodometrically with mass spectrometer analyses suggests the error in $\log P_{\text{O}_2}$ to be less than ± 0.02 . Using the capacitance manometer, eight isothermal expansions over the differential pressure ranges of 1-10 Torr gave a mean deviation of 0.35%. Under the experimental conditions normally encountered during oxidation, i.e., $\Delta P \approx 2$ Torr at a total oxygen pressure of about 7 Torr, 16 determinations gave a mean deviation of 0.067%. Based on a consideration of the above errors and on a least squares fit of the data in the single phase σ region (O/Bk < 1.78), the uncertainty in composition is estimated to be ± 0.003 in O/Bk. A least squares fit of the thermodynamic data in the σ region gave an uncertainty, expressed as one standard deviation, of $\Delta \bar{G}(\text{O}_2) \pm 0.27$ kcal. The error in $\Delta \bar{H}(\text{O}_2)$ and $\Delta \bar{S}(\text{O}_2)$ is estimated to be ± 2 kcal and ± 1 e.u., respectively, however, since only the three lowest temperature isotherms were used in the thermodynamic treatment, the error estimates in these partial thermodynamic quantities is of somewhat questionable statistical significance. In the region O/Bk > 1.78 , there is an apparent increased scatter which is related to the decrease in the magnitude of ΔP accompanying oxidation. It is estimated that the errors in this region are not greater than 1.5 times those given above for the low composition region.

SUMMARY

A unique, highly sensitive system for the quantitative monitoring of gas-solid reaction as a function of temperature was constructed and successfully applied to several reactions. These include accurate measurements of equilibria in the system $\text{PrO}_x\text{-O}_2$ using a 1 mg sample; pyrolysis of micro-gram samples of CaCO_3 , and stoichiometry determinations in the CeO_x and BkO_x systems using 1 mg samples. The system was shown to be sensitive to 5×10^{-11} moles of gas and to give reproducible and accurate data.

Oxygen dissociation pressures (10^{-6} - 10^{-20} atm) over the BkO_x oxide system were measured as a function of composition over the range $1.55 < \text{O/Bk} < 1.95$, at temperatures from 852 to 1150°C. These, plotted isothermally against O/Bk, define two grossly nonstoichiometric fields separated by a diphasic region. In addition, a narrow two phase region with mean composition $\text{BkO}_{1.917}$ was found for the 852 and 925°C isotherms.

The derived enthalpy and entropy relations to composition were shown to be similar to those reported for the CeO_x system. The diphasic field at $\text{BkO}_{1.917}$ is analagous to a similar narrow field recently reported for the $(\text{Ce,U})\text{O}_{2-x}$ system.

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APPENDIX A

CAPACITANCE MANOMETER SYSTEM II

The success of the initial unit and the obvious need for certain modifications resulted in the construction of the system shown in Figure A-1. All tubing is stainless steel, valves are bellows sealed, and the plate mounted system is within two water jacketed copper boxes and an outer aluminum box. Two-inch thick slabs of Styrofoam insulate each of the copper boxes. Bakelite valve extension rods protrude through the top of the aluminum cover. After initial thermostating, the inner box can be isolated from the outer one, and the water flow maintained only for it. The entire box system weighs approximately 120 lbs., providing a substantial heat sink for smoothing of small temperature fluctuations.

The box system is built into the wall of a fume hood so that the two sample tubes enter the furnace within the hood. The use of dual tubes in the hot zone will be useful for certain types of experiments where the pressure rise due to heating will not cause a change in the differential pressure. Although this will be strictly true only for the case where the differential pressure is initially zero, a large, though incomplete nulling of the heat effect (when differential $P \neq 0$) will be often desirable. Variable control of the nulling capability can be achieved by varying the hot zone volume of one of the tubes via magnetic positioning of the filler rod. Provision is made for adjusting volume (and, therefore, sensitivity) in the ratios 1:10:100.

FIGURE 1A. Improved capacitance manometer system.

APPENDIX BBkO_x RUN PROCEDURES

The run procedure for which reference to Figure B-1, showing valve designations can be made, is outlined as follows:

Equilibration

A. Heat up after oxidation at 500°C

1. Pump V_x to $< 9 \times 10^{-6}$ Torr with X1 and R1 closed and R3, X4, X3, X2 open.
2. Close X3 and admit the desired CO/CO₂ ratio into 80 cc ballast. Record the total pressure using the cathetometer.
3. Close R3 and X4. Pump out the line to R1, R3.
4. Slowly open X3 and close immediately after to admit gas to the furnace. Start the programmer.
5. Be sure R3 is closed and RX is open. Open R1 to be ready for flushing procedure at temperature.

B. Equilibration at Temperature

Prior to attaining temperature the 80 cc ballast contains the CO/CO₂ supply, X1 is closed, V_R is evacuated, RX is open, and the sample tube contains CO/CO₂.

1. Check that R3 is closed and RX is open. Open R1. Open X1 while observing the recorder with 1 Torr full scale. Open it slowly enough that $\Delta P < 0.5$ Torr is observed. Pump to 15 μ on the Pirani guage.
2. Close X1. Open X3, admitting CO/CO₂ to the sample. Close X3.
3. Hold gas over the sample for 15 minutes.
4. Go through Steps 1 to 3 five times at temperature. Be sure during the last two equilibrations that temperature is constant to within 0.005 mV.

C. Cooling Procedure

(Use the programmer to cool to about 600°C and then put on set point.)

FIGURE 1B. Capacitance manometer system. The dashed lines represent the thermostated copper box. X and R on the manometer refer to the sample and reference sides, respectively.

1. While last CO/CO₂ flush is in furnace, close R1 and open R3. Open X4 (be sure X3 is closed) to start to pump the 80 cc ballast. After ~ 10 minutes pumping, drop the LN₂ trap with the stopcock above the trap closed. Warm the trap with the heat gun. After the CO₂ is sublimed, replace the trap and resume pumping.
2. After 15 minutes of flush (total), open X1 slowly and then close it immediately. Open X3 slowly and pump the furnace and 80 cc ballast to 9×10^{-6} Torr.
3. Valve off X2 and R3.
4. Start to cool at 10°/min.
5. Pump V_R through R1 to 9×10^{-6} Torr while cooling to 500°C. (Be sure RX is open, X1 closed.) Go to #1, Oxidation Procedure.

Oxidation

1. While cooling from temperature to 500°C, pump V_R to 9×10^{-6} Torr.
2. When V_R has been pumped down, open R3, X4, X3, and pump the entire system during the remaining cooling time. Be sure the pressure here is $\leq 9 \times 10^{-6}$ Torr at 500°C.
3. Close R1.
4. Be sure X1 is closed. Now close X2 and X3.
5. Fill the 80 cc ballast with ~ 10 Torr O₂.
6. Set the bridge zero and close RX.
7. Be sure X2 is closed and open X1.
8. Slowly open X3 to bleed in ~ 7.4 Torr O₂ from the 80 cc ballast.
9. Close X3 and start pumping out the ballast.
10. After checking the zero drift on the recorder, obtain P_b by nulling the manometer output. Drift should be ± 0 for a 2 minute period.*

*If relative volumes are not to be determined, open RX slowly and immediately close X1. Slowly open X3 to pump V_X down to 9×10^{-6} Torr. Go to Equilibration Procedure.

Relative Volumes

1. After the oxidation, and with X1 dosed, evacuate with X2, X3, and X4 open to $< 9 \times 10^{-6}$ Torr.
2. Close X3 and X2.
3. Open X1 and read the pressure after a zero drift is achieved.
4. Open X2 and again after achieving a zero drift, read the pressure.
5. Pump out V_X to 9×10^{-6} Torr.
6. Close X1, X3 and fill the 80 cc ballast with the new CO_2/CO charge. Record the pressure of CO_2/CO using the H_g manometer and close X4, R3.
7. Open X3 slowly to admit the gas to the sample. After fully opening X3, close X3 immediately.
8. Go to Equilibration Procedure.

APPENDIX C

TABULATION OF RESULTS

852°C Isotherm

<u>Run</u>	<u>CO₂/CO</u>	<u>-log p_{O₂} (atm)</u>	<u>-ΔG_{O₂} (kcal/mole O₂)</u>	<u>O/Bk</u>	<u>%Bk</u>
17	100.33	13.159	67.70	1.9273	96.1
18	100.33	13.159	67.70	1.9300	96.0
20	0.3359	18.102	93.18	1.6561	95.9
25	0.0994	19.160	98.63	1.5700	95.7
28	0.9854	17.168	88.37	1.7174	95.5
31	0.9854	17.168	88.37	1.7171	95.3
35	7.9850	15.350	79.02	1.8372	95.1
39	473.50	11.804	60.76	1.9763	94.9
44	2.1740	16.480	84.83	1.7609	94.7
49	1.4943	16.806	86.51	1.7408	94.4
54	1.8420	16.624	85.57	1.7531	94.2
63	30.098	14.198	73.08	1.8690	93.9
68	98.764	13.166	67.77	1.9270	93.7
73	0.2003	18.551	95.50	1.6229	93.5
76	0.0693	19.473	100.2	1.5684	93.4
81	0.5872	17.617	90.69	1.6969	93.2
85	51.842	13.725	70.65	1.8821	93.0
88	70.899	13.454	69.25	1.9025	92.9
90	78.071	13.370	68.82	1.9044	92.8
94	2.5421	16.344	84.13	1.7716	92.7
96	119.17	13.002	66.93	1.9303	92.6
98	119.17	13.002	66.93	1.9074	92.5
101	122.70	12.977	66.80	1.9271	92.3
102	0.3801	17.995	92.63	1.6678	92.3
107	3.8025	15.995	82.33	1.8186	92.1
113	189.45	12.600	64.86	1.9404	91.8
117	469.61	11.811	60.80	1.9675	91.7
122	94.615	13.203	67.96	1.9078	91.0

<u>Run</u>	<u>CO₂/CO</u>	<u>-log p_{O₂} (atm)²</u>	<u>-ΔG_{O₂} (kcal/mole O₂)</u>	<u>O/Bk</u>	<u>%Bk</u>
124	37.921	14.000	72.05	1.8787	90.8
126	15.172	14.793	76.15	1.8723	90.6
128	5.2929	15.707	80.86	1.8290	90.4
145	1002.8	11.152	57.41	1.9839	87.9
154	0.9970	17.157	88.32	1.7192	87.5
155	0.9970	17.157	88.32	1.7219	87.4
161	15.557	14.771	76.03	1.8621	87.2

925°C Isotherm

29	0.9854	15.570	85.35	1.7176	95.5
41	473.50	10.206	55.95	1.9737	94.8
46	2.1740	14.882	81.58	1.7619	94.6
51	1.4943	15.208	83.36	1.7405	94.3
55	1.8420	15.026	82.37	1.7542	94.2
58	2.9917	14.605	80.06	1.8070	94.1
60	30.098	12.600	69.07	1.8673	94.0
67	98.764	11.568	63.41	1.9259	93.7
71	0.2003	16.954	92.93	1.6255	93.6
78	0.0693	17.876	97.99	1.5740	93.3
82	0.5872	16.019	87.81	1.6951	93.1
86	51.842	12.128	66.48	1.8840	93.0
89	70.889	11.856	64.99	1.9844	92.9
91	78.071	11.772	64.53	1.9048	92.8
95	2.5421	14.746	80.83	1.7727	92.7
97	119.17	11.405	62.51	1.9277	92.6
99	119.17	11.405	62.51	1.9071	92.5
103	0.3801	16.397	89.88	1.6681	92.3
106	3.803	14.397	78.92	1.8135	92.5
114	189.45	11.002	60.31	1.9406	91.9
119	469.61	10.213	55.99	1.9641	91.7
121	94.615	11.605	63.61	1.9072	91.1
123	37.921	12.399	68.00	1.8808	90.9

Run	CO_2/CO	$-\log p_{\text{O}_2}$ (atm) ²	$-\Delta G_{\text{O}_2}$ (kcal/mole O_2)	O/Bk	%Bk
125	15.172	13.195	72.33	1.8549	90.7
127	5.2929	14.109	77.34	1.8260	90.5
129	0.0326	18.531	101.58	1.5584	90.2
146	1002.8	9.554	52.37	1.9768	87.9
151	13.616	13.289	72.84	1.8585	87.7
152	13.616	13.289	72.84	18.559	87.5

996°C Isotherm

14a	9.987	12.193	70.76	1.8415	96.8
14b	9.987	12.202	70.79	1.8391	96.5
15a	100.33	10.174	59.08	1.9034	96.3
15b	100.33	10.189	59.13	1.8954	96.2
21	0.3359	15.054	87.68	1.6644	95.9
24	0.0994	16.185	93.97	1.5841	95.7
27	0.9854	1.4192	82.40	1.7194	95.6
34	7.9850	12.375	71.85	1.8293	95.2
38	473.50	8.828	51.26	1.9667	94.9
43	2.1740	13.505	78.41	1.7945	94.7
48	1.4943	13.830	80.30	1.7430	94.4
56	1.8420	13.649	79.25	1.7569	94.1
62	30.098	11.222	65.16	1.8688	93.9
66	98.764	10.190	59.17	1.9154	93.8
72	0.2003	15.576	90.44	1.6311	93.5
77	0.693	16.498	95.79	1.5795	93.3
83	0.5872	14.642	85.01	1.6955	93.1
87	51.842	10.750	62.44	1.8821	92.91
92	78.071	10.394	60.35	1.9062	92.8
100	119.17	10.027	58.22	1.9059	92.5
104	0.3801	15.019	87.21	1.6693	92.2
108	3.8025	13.019	75.59	1.8136	92.1
115	189.45	9.624	55.88	1.9327	91.8
120	469.61	8.836	51.30	1.9613	91.7

Run	CO_2/CO	$-\log P_{\text{O}_2}$ (atm)	$-\Delta G_{\text{O}_2}$ (kcal/mole O_2)	O/Bk	%Bk
130	0.0326	17.153	99.60	1.5665	89.7
147	1002.8	8.177	47.48	1.9741	87.9
149	64.531	10.560	61.31	1.8935	87.8
162	10.873	12.106	70.29	1.8504	87.2
163	19.597	11.595	76.32	1.8617	87.1
164	8.7060	12.299	71.42	1.8468	87.1

1075°C Isotherm

32	0.9854	12.829	79.13	1.7187	95.3
36	7.9850	11.012	67.92	1.8285	95.0
40	473.50	7.466	46.05	1.9583	94.8
45	2.1740	12.142	74.89	1.7924	94.6
50	1.4943	12.468	76.90	1.7454	94.4
53	1.8420	12.286	75.78	1.7878	94.2
61	30.098	9.860	60.81	1.8642	93.9
65	98.764	8.828	54.45	1.9060	93.8
70	0.2003	14.213	87.67	1.6358	93.6
75	0.0693	15.135	93.35	1.5892	93.4
80	0.5872	13.279	81.90	1.6915	93.2
105	0.3801	13.657	84.23	1.6752	92.2
109	3.8025	11.657	71.90	1.8092	92.0
116	189.45	8.262	50.96	1.9254	91.8
132	0.0326	15.791	97.40	1.5759	89.5
148	64.531	9.197	56.73	1.8918	87.8
160	15.557	10.433	64.35	1.9576	87.2

1150°C Isotherm

19	100.33	7.660	49.88	1.9087	96.0
22	0.3359	12.611	82.11	1.6746	95.8
23	0.0994	13.669	89.00	1.6212	95.7
26	0.0985	11.676	76.02	1.7251	95.6

<u>Run</u>	<u>CO₂/CO</u>	<u>-log P_{O₂} (atm)</u>	<u>-ΔG_{O₂} (kcal/mole O₂)</u>	<u>O/Bk</u>	<u>%Bk</u>
42	2.1740	10.989	71.55	1.7907	94.7
47	1.4943	11.314	73.67	1.7811	94.5
52	1.8420	11.133	72.48	1.7863	94.3
64	30.098	8.706	56.69	1.8644	93.8
69	98.764	7.674	50.00	1.9061	93.6
74	0.2003	13.060	85.03	1.6492	93.5
79	0.0693	13.982	91.04	1.6063	93.2
84	0.5872	12.126	78.95	1.7036	93.0
93	78.071	7.878	51.29	1.8876	92.7
110	3.8025	10.503	68.39	1.8090	92.0
144	0.0326	14.368	95.30	1.5827	88.0
150	64.531	8.044	52.37	1.8884	87.7
153	13.616	9.395	61.17	1.8520	87.5
159	15.557	9.279	60.42	1.8552	87.3

Isoplethal (-log P_{O₂}) Data from Figure 12

<u>O/Bk</u>	<u>1150°C</u>	<u>1075°C</u>	<u>996°C</u>	<u>925°C</u>	<u>852°C</u>
1.58	14.72	15.41	16.41	17.75	19.27
1.60	14.18	14.93	16.04	17.37	18.90
1.62	13.70	14.53	15.74	17.07	18.62
1.64	13.29	14.17	15.43	16.78	18.33
1.66	12.89	13.81	15.13	16.48	18.04
1.68	12.51	13.48	14.52	16.18	17.75
1.70	12.13	13.15	14.52	15.88	17.45
1.72	11.78	12.84	13.22	15.56	17.15
1.74	11.45	12.54	13.92	15.25	16.84
1.76	11.45	12.40	13.62	14.93	16.52
1.78	11.32	12.40	13.52	14.70	16.22
1.80	10.70	11.88	13.33	14.70	16.00
1.82	10.11	11.23	12.68	14.19	15.97
1.84	9.50	10.62	12.03	13.62	15.29

<u>O/Bk</u>	<u>1150°C</u>	<u>1075°C</u>	<u>996°C</u>	<u>925°C</u>	<u>852°C</u>
1.86	8.91	10.02	11.41	12.94	14.63
1.88	8.32	9.46	10.80	12.31	13.99
1.90	7.76	8.90	10.21	11.70	13.37
1.91	7.48	8.63	10.10	11.50	13.12
1.92	---	8.47	10.10	11.50	13.12
1.93	---	8.12	9.87	11.38	13.08
1.94	---	7.89	9.57	11.09	12.76
1.96	---	7.53	8.90	10.48	12.13
1.98	---	---	~7.0	~9.0	~11.4

Derived Thermodynamic Data

<u>O/Bk</u>	<u>$-\Delta\bar{G}_0$ (925°C)</u> <u>(kcal/mole O₂)</u>	<u>$-\Delta\bar{H}_0$</u> <u>(kcal/mole O₂)</u>	<u>$-\Delta\bar{S}_0$</u> <u>(cal/deg/mole O₂)</u>
1.58	~ 96	129.5	~ 28
1.60	94.3	130.3	30.1
1.62	93.2	131.3	31.8
1.64	91.8	132.2	33.7
1.66	90.4	132.6	35.3
1.68	88.8	133.6	37.3
1.70	87.2	133.6	38.7
1.72	85.0	133.6	40.6
1.74	83.7	133.2	41.3
1.76	81.8	132.2	42.1
1.78	80.4	114.0	28.1
1.80	80.4	114.0	28.1
1.82	78.1	150.0	60.0
1.84	74.7	148.6	61.7
1.86	71.2	146.7	63.1
1.88	67.8	145.4	64.8
1.90	64.4	144.0	66.4
1.91	62.9	137.7	62.4
1.92	62.9	137.7	62.4
1.93	62.3	146.3	70.1
1.94	60.4	146.7	71.2
1.98	~50	~158	~90