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Report

THE DETERMINATION OF OXYGEN/METAL RATIOS FOR URANIUM, PLUTONIUM AND (U.Pu) OXIDES

Pu

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by

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ABSTRACT

Non-stoichiometric uranium oxides can be analysed by reduction to $UO_{2.00}$ with CO and measurement of the CO_2 produced. Recent thermodynamic data supports the validity of this method and also establishes the conditions for extending similar methods to the analysis of substoichiometric plutonium oxides and to mixed uranium-plutonium oxides. The theoretical bases of the method and recent practical developments are discussed. The accuracy of analyses obtainable by gas handling methods is illustrated by typical recent results, and possible future modifications are outlined. Oxygen/metal ratios can be determined to ± 0.001 in the case of hyperstoichiometric MO_{2+x} oxides, and to ± 0.002 in the case of hypostoichiometric MO_{2-x} oxides.

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1. $\Delta\bar{G}_{(O_2)}$ versus O/M ratio for UO_{2+x}, PuO_{2-x}, $U_{0.89}\,Pu_{0.11}\,O_{2\pm x}$ and $U_{0.70}\,Pu_{0.30}\,O_{2\pm x}$ at 850°C.
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Introduction

Uranium oxides exhibit a range of non-stoichiometric behaviour between UO_2 and U_3O_8. Plutonium forms non-stoichiometric oxides between Pu_2O_3 and PuO_2, based on oxygen ion vacancies. Oxygen-rich preparations of PuO_2 hold excess oxygen only by adsorption on the surface; the oxygen adsorbed is directly proportional to the surface area and the pressure of the oxygen(2). Mixed (U,Pu) oxides also form non-stoichiometric oxides with compositions between MO_{2-x} and MO_{2+x} where x depends upon the percentage of Pu in UO_2. The value of x in MO_{2-x} is a maximum when all the Pu in the (U,Pu) oxide is in the trivalent state.

Oxygen/Uranium Ratios

Oxygen/uranium ratios can be determined by several methods:

(a) Ignition of the oxide to U_3O_8 is widely used. Care has to be taken that the composition of the ignited sample is truly O/U = 2.667. Unfortunately, weight changes of significance are small; a change of 0.01 in O/U ratio in an 0.5g sample causes a weight change of only 0.3mg.

(b) Polarographic analysis and potentiometric titration depend upon the determination of the U(VI) ions in solution after dissolution of the oxide. Neither of these methods is applicable to oxides with an O/U ratio greater than 2.10 since the concentration of U(IV) ions in solution must be kept high to suppress the second reaction shown below:-

$$UO_2^{++} + e^- \rightleftharpoons UO_2^{+}$$

$$2UO_2^{+} + 2H_2^{+} \rightleftharpoons UO_2^{++} + U(IV) + 2H_2O$$

Producibility of ± 0.0005 for the O/U ratio is quoted by Analytical Chemistry Group, A.E.R.E.(3) Since U(III) reduces water, the method cannot be applied to substoichiometric oxides, UO_{2-x}.

(c) X-ray diffraction is of some value as an analytical technique if the oxide sample is a well crystalline material. A change in O/U ratio of 0.01 is accompanied by a change in lattice parameter of 0.0013Å

(UO_2, a = 5.4708Å; $UO_{2.25}(U_4O_9)$ a = 5.438Å). It is possible to measure the lattice parameter of a well crystalline uranium oxide to ± 0.0002Å using the high angle lines from the powder diffraction photograph and applying the Nelson and Riley correction(3a). It should therefore be possible to determine O/U ratios to ± 0.005 for well crystalline materials which have been annealed at high temperatures (>1200°) and successfully quenched. Samples annealed at lower temperatures are not so well crystalline and it is not possible to measure lattice parameters to better than ± 0.0005Å corresponding to an error in O/U ratio of ± 0.01; further, dissociation into two phases may occur on cooling.

(d) A method widely used in Solid State Chemistry Group, A.E.R.E., Harwell, for determining O/U ratios is reduction of the oxide to stoichiometric UO_2 with CO, followed by measurement of the CO_2 produced, using a gas handling system(1).

(e) All of the methods outlined above involved the destruction of the oxide. There have been instances when a knowledge of the O/U ratio of an oxide is required prior to subsequent experiments (e.g. neutron diffraction studies on UO_{2+x}) and verification during the experiment that the O/U ratio of the oxide has not altered. Measurement of the oxygen potential of oxides using a high temperature galvanic cell leads to a non-destructive method for determining O/U ratios(4,5,5a). The e.m.f. of the cell, using a Ni,NiO reference electrode was plotted against O/U ratio as determined by the CO reduction method.

Oxygen/Plutonium Ratios

(a) The O/Pu ratio of substoichiometric PuO_2 has been determined by measuring the weight change on oxidation at 900° to PuO_2; a change in O/Pu ratio of 0.01 is accompanied by a weight change of 0.3 mg. in an 0.5g. sample of oxide. Measurement of change of weight is satisfactory for a pellet of low surface area but for a powder of high surface area the results may be misleading due to surface adsorption of oxygen(2).

(b) The substoichiometric oxide may be oxidised to PuO_2 with a measured excess of oxygen in a gas handling system. If the oxide is a powder with a high surface area, the oxidation to PuO_2 can be followed by a CO reduction at 850°C to remove adsorbed oxygen, and measurement of the CO_2 produced. This method has been used at Harwell(6).

(c) An e.m.f. cell can be used to determine O/Pu ratios non-destructively once the e.m.f. has been plotted against O/Pu ratio(6).

Oxygen/(Uranium, Plutonium) Ratios

(a) The O/M ratio of mixed oxides has been determined by measuring the weight change on oxidation in air at 750°, followed by H_2 reduction (flow method) at 700°. The difference in weight determines the O/M ratio assuming the final composition to be $MO_{2.00}$(7).

(b) A method used at D.E.R.E., Dounreay,(8,9) has been to measure the lattice parameter of the oxide and relate this to O/M ratio by a ternary or "fan" plot. The fan is constructed from the Vegard's Law line for PuO_2/UO_2, PuO_2/U_4O_9 and $PuO_{1.62}/UO_2$. Whilst it has been shown conclusively that Vegard's Law is obeyed for PuO_2/UO_2, there is no theoretical justification for Vegard's Law being obeyed either for PuO_2/U_4O_9 or $PuO_{1.62}/UO_2$. Some recent work at Harwell(6,10) suggests that the validity of Vegard's Law for the latter two cases is doubtful. Determinations of O/M ratios by this method are probably not more accurate than ± 0.02.

(c) O/M ratios have been determined by Markin and Bones(6), using a gas handling apparatus. Substoichiometric U,Pu oxides have been oxidised to MO_{2+x} with a measured volume of oxygen, followed by CO reduction at 850° to $MO_{2.00}$ (10/1: CO/CO_2) and collection of the CO_2 produced. The O/M ratio of superstoichiometric oxides has been determined by CO reduction at 850°.

(d) An e.m.f. cell can be used as in the case of O/U and O/Pu ratios(6).

It is the purpose of this report to describe a typical gas handling apparatus which can be used for determining O/M ratios of UO_{2+x}, PuO_{2-x} and $(U,Pu)O_{2\pm x}$ by oxidation and CO reduction.

Theoretical Basis of Gas Reduction Method

Although the CO_2/CO ratio of 1/10 at 850° was chosen arbitrarily, thermodynamic data for UO_2, obtained from e.m.f. cells, has shown that this choice of gas mixture produces an O/U ratio very close to 2.00. A CO_2/CO ratio of 1/10 at 850°C corresponds to a $\Delta\bar{G}_{(O_2)}$ ($= RT\ln P_{(O_2)}$) value of -104 Kcals. Several pellets of UO_2 which had been equilibrated with a CO_2/CO ratio of 1/10 at 850° for 16 hours have been placed in the high temperature galvanic cell, Ni,NiO/Anionic Electrolyte/UO_2. From e.m.f. measurements at temperatures between 600° and 1000°, $\Delta\bar{G}_{(O_2)}$ for $UO_{2.00}$ has been found to vary between -103 and -108 Kcals at 850°C(5). Table I shows the variation of $\Delta\bar{G}_{(O_2)}$ for CO_2/CO mixtures and O/U ratios.

TABLE I

$\Delta\bar{G}_{(O_2)}$ for CO_2/CO mixtures and O/U ratios

CO_2/CO	$-\Delta\bar{G}_{(O_2)}$ Kcals	O/U ratio
1/10	104	2.00
1/2	91	2.0005
1/1	88	2.0007
2/1	86	2.0010
5/1	83	2.0014

The results show that values of $\Delta\bar{G}_{(O_2)}$ close to the expected values are actually obtained by this reduction procedure. Similar results have been obtained for PuO_2 and $(U,Pu)O_2$ reduced with a 1/10, CO_2/CO mixture at 850°C(6). The composition reached should not be critically dependent on the composition of the gas used, since $\Delta\bar{G}_{(O_2)}$ varies very steeply with composition in this region. Fig. 1 shows a plot of $\Delta\bar{G}_{(O_2)}$ versus O/U ratio,(5) O/Pu ratio and O/U,Pu ratio;(6) it can be seen that close to $MO_{2.00}$, the plot becomes very nearly vertical. For the mixed oxides in particular, an enormous change in $\Delta\bar{G}_{(O_2)}$ occurs between $MO_{1.99}$ and $MO_{2.01}$; the obvious inference is that the stoichiometric composition occurs at the steepest part of this curve, close to $\Delta\bar{G}_{(O_2)} = -100$ Kcals.

Experimental Development

The determination of O/M ratios of superstoichiometric uranium and (U,Pu) oxides by reduction to stoichiometric $MO_{2.00}$ with CO and measurement of the CO_2 formed has the advantage over other methods that accurate measurements can be made on specimens as small as 50 mg. for O/M ratios below 2.05 or 5mg. for higher O/M ratios. The small quantities of CO_2 formed can be measured on a McLeod gauge at several different pressures if the volume of the gas handling system can be varied, e.g. by a mercury gas burette. Roberts and Harper$^{(1)}$ used hydrogen and CO for reducing UO_{2+x} but, as reported in their paper, a correction for adsorption of H_2O on the walls of the apparatus is necessary if H_2 is used. CO reductions are therefore preferable. The CO_2 produced by the reduction was collected at a total gas pressure of $\frac{1}{4}$ to $\frac{1}{2}$ atm; the O/U ratios were sometimes low indicating incomplete trapping of CO_2. To investigate the cause of incomplete trapping of CO_2, mixtures of CO/CO_2 (total pressure $\frac{1}{2}$ atm.) were made up and circulated by a pump through an empty specimen holder and through a U tube trap cooled in liquid oxygen. The trap was then isolated and after pumping away the CO, allowed to return to room temperature. The CO_2 was measured on a manometer. It was found that the CO_2 was not completely recovered by this technique, as is shown in Table II, run (a) and (b).

Table II

Recovery of CO_2 from CO/CO_2 mixtures

Run	Mixture			ccs. CO_2 recovered	%
	ccs. CO	ccs. CO_2	Pressure		
(a)	92.2	9.79	30.1 cm.	8.81	90.0
(b)	97.6	8.79	31.7 cm.	8.05	91.6
(c)	90.2	7.68	28.9 cm.	7.66	99.7
(d)	84.9	7.66	31.2 cm.	7.67	100.1

In runs (c) and (d), after circulating the gas through the empty specimen holder for 15 minutes, the gas was pumped slowly through the trap at low pressure, controlling the pumping on a stop cock between the trap and the empty specimen holder. In these runs there is good agreement between the amount of CO_2 put into the mixture and the amount trapped. The probable reason for this result is that the mean free path of the molecules is much greater at low pressures so that collection of the CO_2 is more efficient if the gas is passed through the cold trap at low pressures.

In another series of experiments in an apparatus designed for analysis of plutonium carbides,$^{(11)}$ a known weight of calcite was heated to 800-900° in a gas handling system and the CO_2 evolved was trapped. In run (a) (Table III) calcite was heated in an evacuated specimen holder connected to a trap cooled in liquid oxygen and it was found that the volume of CO_2 collected was close to the expected amount; the CO_2 was condensed at a low pressure as it was formed from the decomposition. When this was repeated with oxygen present (run (b)) to simulate conditions used for analysis of carbides by conversion of carbon to CO_2, about 80% of the theoretical CO_2 was collected. The trap had been cooled for about 1 hour and the gas moved back and forth through the trap by raising and lowering a mercury column. In run (c), the calcite was heated with oxygen but the trap was isolated; the gas mixture was pumped through the trap at low pressure at the end of the decomposition. 99% of the theoretical amount of CO_2 was collected.

Table III

Recovery of CO_2 liberated from calcite

Run	Mass of Calcite	Mass calc. from CO_2	%
(a)	23.60 mg.	23.35 mg.	98.9
(b)	24.90 mg.	19.67 mg.	79.0
(c)	27.42 mg.	27.08 mg.	98.0

Crossley and Phillips(12) used a narrow bore multiloop trap to condense all the CO_2 formed in carbon analysis with a flow method. Drummond and Sinclair(14), using a thermogravimetric method with a gas flowing over the sample, had incomplete reduction of U_3O_8 specimens at 800° but this may have been due to incomplete removal of reaction products (H_2O and CO_2) from the material by the gas flow method. It may be noted that reaction in a stream of <u>pure</u> CO is not, in fact, the ideal method. Roberts, Walter and Wheeler(13) showed that in order to avoid carbon deposition on UO_2 during CO reduction, with consequent CO_2 production from a side reaction, the ratio of CO_2/CO should be not less than 1/100.

Carbon from the disproportionation reaction of CO can be estimated by oxidation of the oxide and collection and measurement of the CO_2 formed.

<u>Gas Handling System</u>

A typical gas handling system is shown in Fig. 2. All volumes can be calibrated using the grade A burette C. B is the sample holder; this may be either a straight tube with a cooled black wax joint (B1) or a tube with a side arm (B2) connected to a gas circulating pump. If type B1 is employed, the mercury in the gas burette C must be raised and lowered every 30 minutes in order that thermal diffusion of gases and non-mixing of gas through tap J does not affect the final result. Type B2 including a circulating pump, is preferred if a high degree of accuracy is required because the pump overcomes thermal diffusion and non-mixing problems; the linear gas flow rate over the sample should be not less than 1cm/sec. CO is let into the volumes B and C with taps F and G closed. After the reduction is complete, tap F is slightly opened and the CO/CO_2 mixture pumped out through the trap cooled in liquid oxygen, with tap H fully open. The rate at which the gas is removed can be judged by the rate of rise of mercury in the manometer I which should be not more than about 1cm/minute. The system should then be pumped for about 30 minutes to ensure that any CO adsorbed on the surface of the oxide and solid CO_2, is removed. With the reaction vessel B isolated and tap H closed, the trap can be allowed to reach room temperature; the CO_2 may be measured on either the manometer or, if the volume is small, on the McLeod gauge.

For small quantities of CO_2 (~4 mg), a trap consisting of a U tube, 5 mm. bore, immersed in liquid oxygen, is sufficient but in order to completely trap larger amounts of CO_2, it is preferable that the U tube is filled with glass beads in order to stop flakes of CO_2, which may break away from the walls of the tube, being carried out of the tube with the CO gas stream.

Large specimens may be weighed directly into the sample tube B but for small quantities it is better to weigh a specimen into a small silica cup and transfer the cup and contents to the tube B.

The same apparatus may be used for complete or partial oxidation of oxides; in this case the gas circulation pump will not be needed.

The time needed for complete reduction by the CO method depends upon the particle size of the oxide; a powder of small particle size (surface area 1.2m^2/g) may require only ½ hour, whereas a 0.5g. pellet may have to be left overnight to ensure complete reduction. Faster reduction by CO might be achieved at higher temperatures, but the use of silica tubes above 900°C is not recommended because silica becomes porous. Reduction can be checked by adding fresh CO, but, the complication of the $2CO \rightarrow CO_2 + C$ reaction may vitiate this; a small blank found in successive doses of CO may be substracted from the CO_2 produced. It is better to reduce a duplicate sample for a longer time to show that no further reduction occurs.

Prior to CO reduction, or to oxidation by measured volumes of oxygen, the sample should be outgassed to remove water vapour and adsorbed gases. The temperature of the sample should be slowly increased until no further outgassing occurs. If an oxide sample has been reduced at some stage in hydrogen, considerable adsorption of hydrogen will have occurred and it may be necessary to heat to 800° to remove the last traces of hydrogen. Care should be taken if the oxide is substoichiometric and has a very low oxygen potential; the oxide will act as an oxygen getter for the vacuum system at only moderate temperatures. In order to overcome this difficulty, the sample should be heated with tap J closed and at frequent intervals the tap should be opened and gases removed.

The apparatus for the purification of CO is shown in Fig. 3. A positive pressure of CO is maintained in section Z and the gas is slowly passed through a liquid oxygen cold trap, over copper gauze at 500° followed by two more liquid oxygen traps. The resulting gas is collected in a 1 litre storage flask and filled to 1 atm. pressure. A blank check on the CO should show that it contains less than 0.1% CO_2. The percentage of CO_2 in the CO should be accurately determined and this figure subtracted from that found in an actual experiment.

The gas handling system may be used to analyse hydrated oxides, e.g. UO_3 hydrates. In this case, the sample must be outgassed at room temperature and then reduced with CO at 800°; this will result in CO_2 and H_2O being trapped when the gases are pumped through the liquid oxygen trap. If the liquid oxygen trap is removed and replaced by a dry ice freezing mixture, the CO_2 will evaporate and the volume may be measured, whilst the H_2O will remain condensed in the trap. Appropriate corrections for the 'cold' volume must, of course, be made. The dry ice freezing mixture must be put round the trap as soon as possible after removing the liquid oxygen trap because at least 30 minutes in dry ice is required to condense the H_2O completely if it volatilises out of the trap.

Typical Results

We report here the results of several series of experiments using the analytical method outlined above in order to illustrate the accuracy usually achieved.

(1) 60 mg. of oxide from about 1 kg. of Malinckrodt UO_{2+x} was analysed by the CO reduction method using a gas handling system. A second sample, 30 mg. in weight, was analysed by the same method in a different gas handling system. A third 20 mg. sample was analysed by measuring the oxygen used to convert it to U_3O_8 by heating to 800° in an excess of oxygen, in a gas handling system. Finally, a pellet

of the Malinckrodt material was made and placed in a high temperature galvanic cell. From the O/U ratio versus e.m.f. calibration plot, the O/U ratio was determined; this calibration plot was compiled from the results of the CO analyses. The results are shown below.

Table IV

Typical results for O/U ratios

Method	Analysis
CO reduction in system 1	2.049
CO reduction in system 2	2.048
Oxidation in U_3O_8 in system 1	2.048
E.m.f. cell	2.048

(2) The O/U ratio of several pellets was estimated by the e.m.f. method and then the U(VI) concentration on dissolution was determined by polarographic analysis. Results are shown in Table V.

Table V

Comparison of e.m.f. and polarographic analyses

Sample	O/U ratio	
	E.m.f. method	Polarographic analysis
P/92	2.051	2.051
P/93	2.051	2.056
P/96	2.018	2.018
P/97	2.023	2.025

The agreement between the e.m.f. method, based on CO reduction, and polarographic analysis is very good except for sample P/93. Samples P/92 and 93 were both prepared from an old stock of Malinckrodt UO_{2+x} and annealed at 900^o overnight in vacuum in the same silica bulb.

E.m.f. measurements confirmed that the O/U ratios were identical, as expected. It appears that some oxidation of P/93 must have occurred after the pellet was removed from the cell and prior to the determination of the U(VI) concentration by polarographic analysis.

(3) Several pellets of PuO_2 were reduced in a batch by hydrogen and a determination of the O/Pu ratio of two pellets from the batch by oxidation to PuO_2 in a gas handling system gave a value of 1.545 ± 0.005. The remaining pellets from the same batch were assumed to have the same O/Pu ratio. Several of the pellets were partially oxidised by a measured volume of oxygen and the partially oxidised pellets were then fully oxidised to PuO_2. By this method it was possible to obtain a check on the O/Pu ratio of the oxide after H_2 reduction and the partially oxidised material. The results are shown in Table VI.

Table VI

Typical results for O/Pu ratios

Sample	H_2 reduced oxide, oxidised to PuO_2	Partial Oxidation, composition deduced from addition of oxygen	Composition deduced by oxidation to PuO_2
X 19	1.545		
X 23		1.871	1.866
X 24		1.712	1.723
X 25		1.618	1.617
X 26		1.577	1.572

Average values for the intermediate compositions are then probably accurate to ± .005 in O/Pu ratio; the greatest uncertainty in this series was the assumption of a constant composition of the fully reduced pellets.

(4) Pellets of UO_2 containing 11% Pu were reduced by very dry hydrogen and then oxidised by a measured excess of oxygen to MO_{2+x}. Finally, the samples were reduced by CO. O/M ratios of two pellets from the same batch were 1.941 and 1.943.

A second reduction of a batch of $U_{0.89}$ $Pu_{0.11}$ O_2 resulted in an average O/M ratio of 1.950. A pellet from the same batch was then oxidised in four stages to $MO_{2.00}$ in the gas handling system by measured volumes of oxygen. The final composition of $MO_{2.00}$ was then checked by oxidation with a small measured volume of oxygen to make the oxide superstoichiometric, followed by CO reduction. The results are shown in Table VII.

Table VII

Typical results for O/(U,Pu) ratios

Sample	H_2 reduction and oxidation to MO_{2+x} followed by CO reduction	Composition after each oxidation step	Final composition, Oxidation to MO_{2+x} and CO reduction
Z1 & 2	$MO_{1.950}$		
Z3		$MO_{1.961}$	
Z3		$MO_{1.980}$	
Z3		$MO_{1.997}$	
Z3		$MO_{2.000}$	
Z3			$MO_{2.003}$

The results show that the final error after four additions of oxygen was only 0.003 in O/M ratio.

Discussion and Future Developments

The general principle of the reduction method consists of fixing the composition so that the $\Delta\bar{G}_{(O_2)}$ value of the reduced oxide is ~104Kcals. A small error in $\Delta\bar{G}_{(O_2)}$ of ± 4Kcals will not measurably alter the O/U ratio. Although it is the standard practice to trap the CO_2 formed by the CO reduction of superstoichiometric oxides, the CO_2 concentration could equally well be measured by other techniques, e.g. infra-red gas analysis or gas chromatography.

The results on duplicates of the same sample suggest that analyses based on the trapping and measurement of the CO_2 produced from the CO reduction, is capable of an accuracy in O/M ratio of ± 0.001 for superstoichiometric oxides. The determination of the O/M ratio of substoichiometric oxides which involves oxidation to MO_{2+x} followed by CO reduction, a two stage process, is probably accurate to ± 0.002 on duplicates of the same sample. Better accuracy could probably be obtained by more accurate calibration and thermostat control of volumes; the gas handling system has not been optimised for accuracy.

It should be possible to develop faster methods for routine analysis by using smaller samples and treating in batches, each in a separate tube, wide enough (1") to avoid gas mixing problems. After outgassing all together, CO could be let into each tube and then each tube isolated by a tap from the gas handling system. Finally, after reduction, each tube could be opened, in turn, to the gas handling system and the CO_2 content analysed either by trapping or by an infra-red gas analyser. Another possible routine analytical technique would be to heat a single sample in a circulating stream of CO, with continuous measurement of CO_2 to determine when reduction was complete; the infra-red gas analyser should be particularly suitable.

The high temperature galvanic cell,(4)(5)(5a) briefly mentioned in the text, affords an excellent method for the non-destructive determination of O/M ratios. An e.m.f. versus O/M ratio calibration plot has to be made before the cell can be used for analysis; O/M ratios may be determined either by the CO reduction method or by polarographic analysis.

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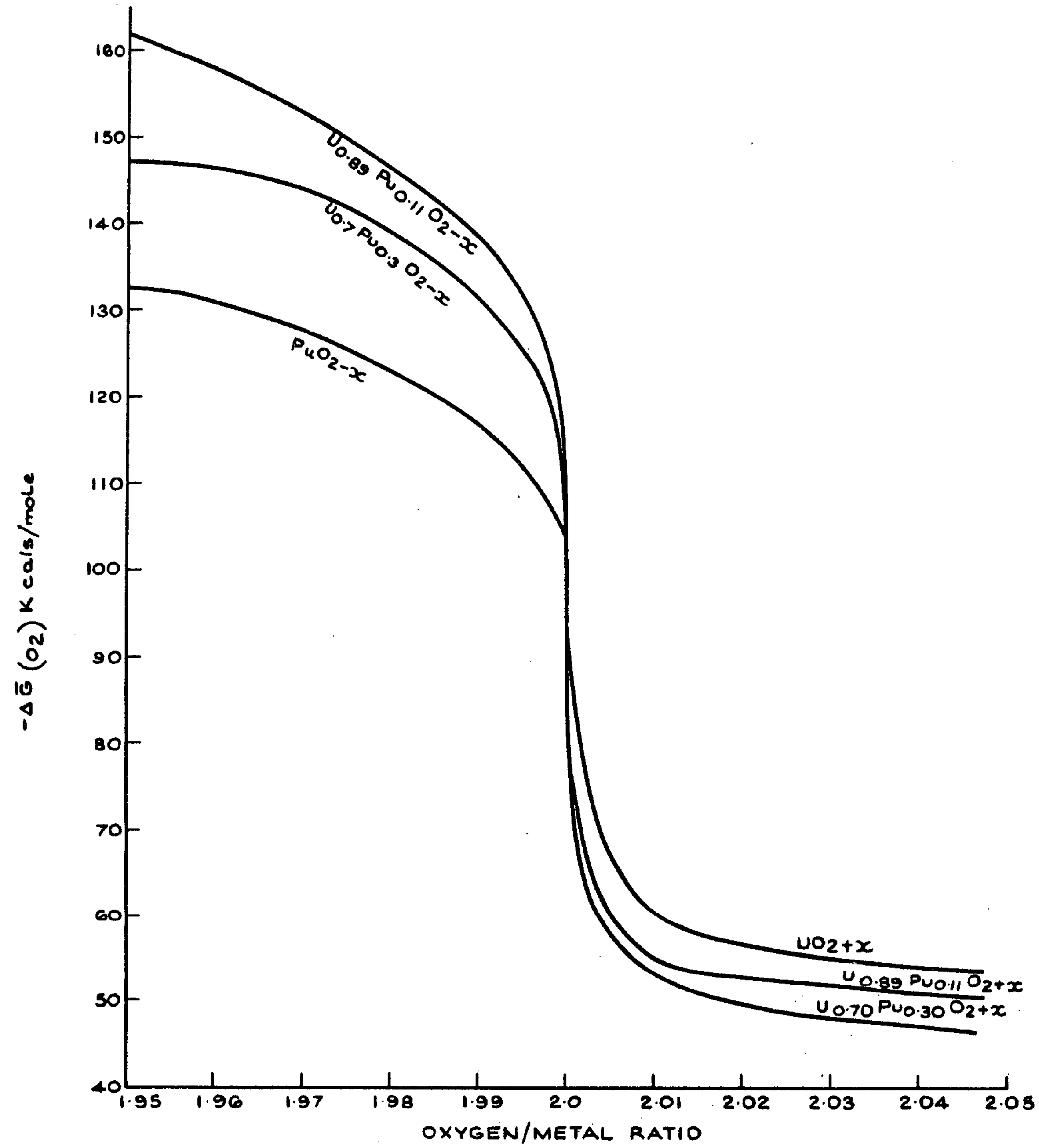

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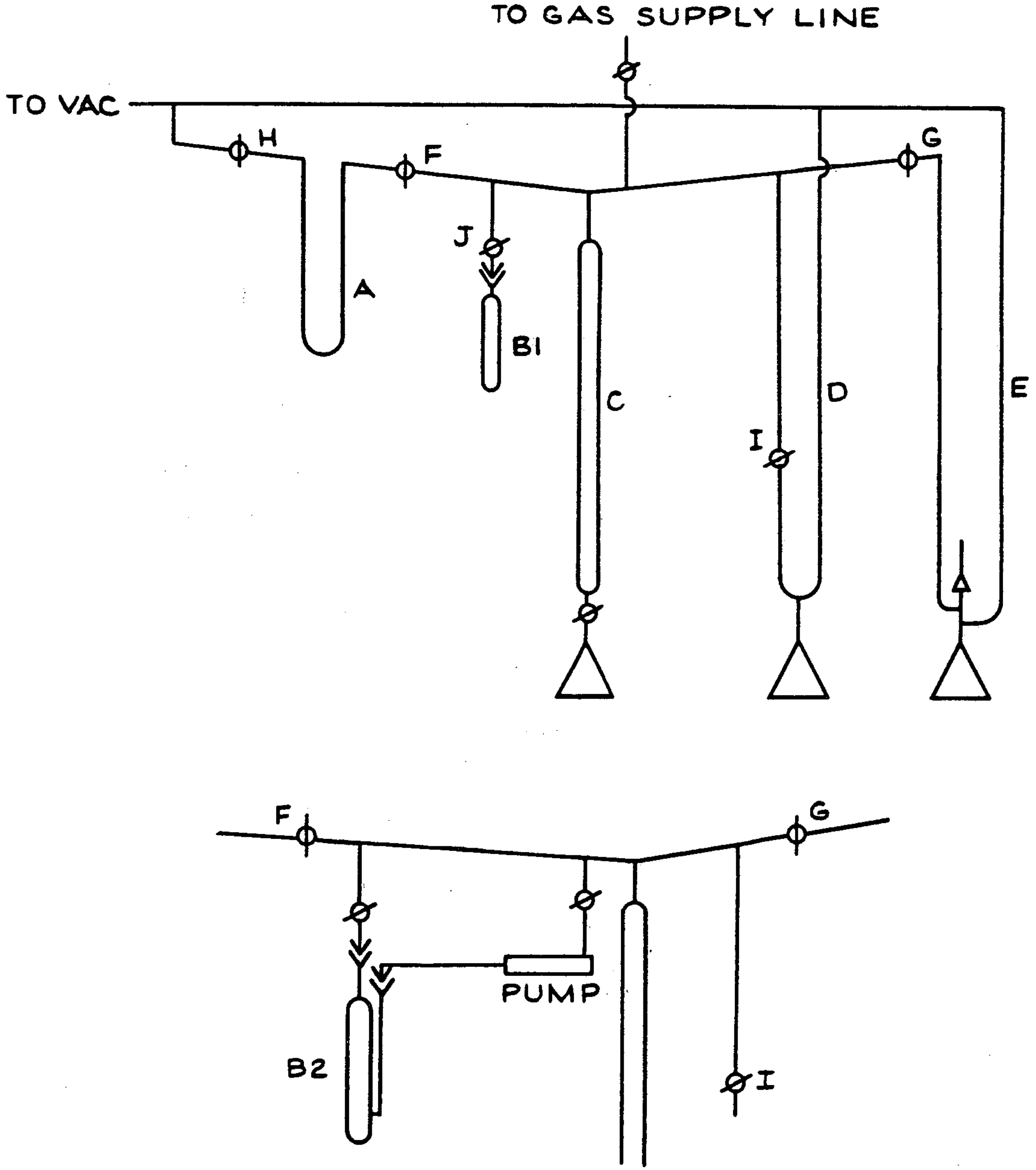
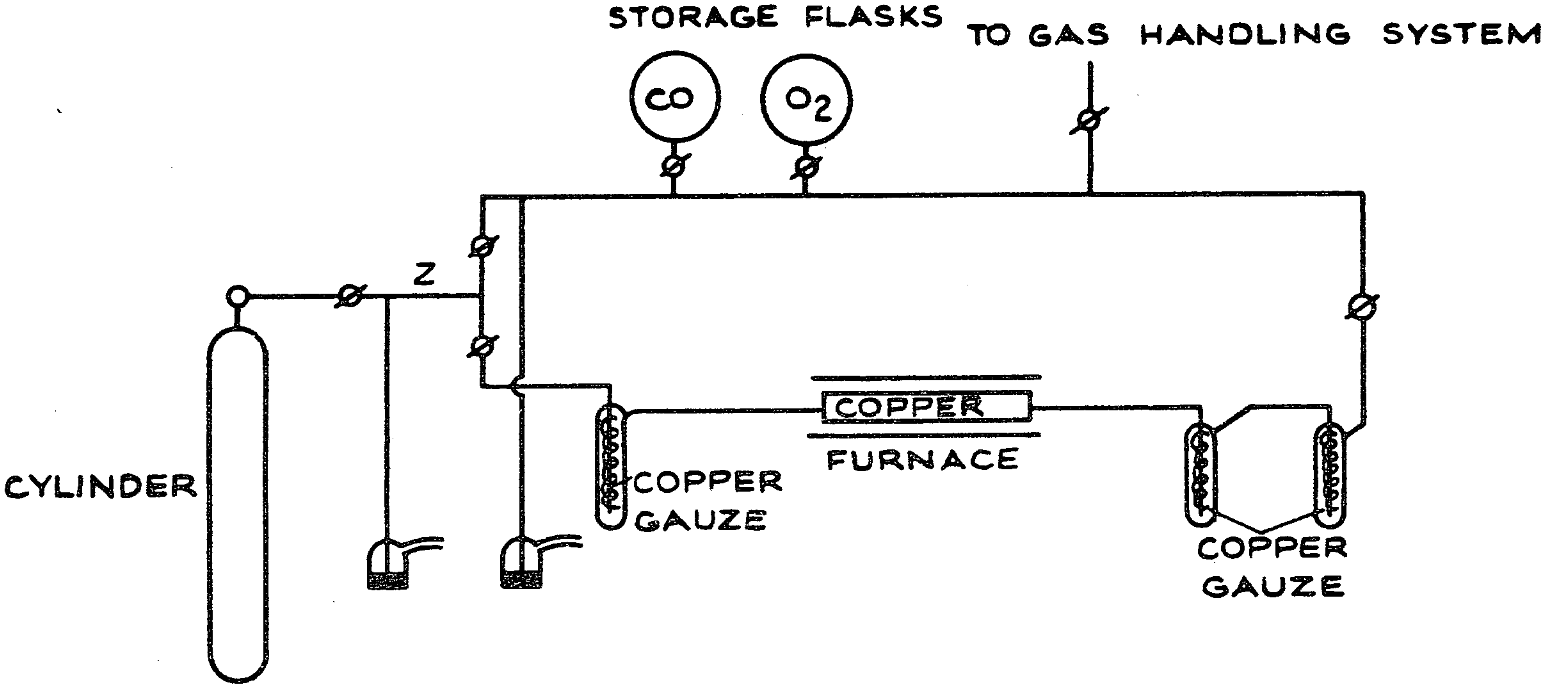
FIG. 1. $\Delta\bar{G}(O_2)$ VERSUS O/M RATIO FOR UO_{2+x} PuO_{2-x} $U_{0·89}Pu_{0·11}O_{2\pm x}$ AND $U_{0·70}Pu_{0·30}O_{2\pm x}$ AT 850°C



A.E.R.E. R4608 FIG. 2. GAS HANDLING SYSTEM.



A.E.R.E. 4608 FIG. 3. CO PURIFICATION SYSTEM AND GAS SUPPLY SYSTEM.

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