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COMMISSION OF THE EUROPEAN COMMUNITIES

**EVAPORATION BEHAVIOR OF
SUBSTOICHIOMETRIC (U, Pu)O₂**

by

R. W. OHSE (Euratom)

and

W. M. OLSON (Los Alamos Scientific Laboratory,
Los Alamos, New Mexico, USA)

1971



Joint Nuclear Research Centre
Karlsruhe Establishment - Germany

European Institute for Transuranium Elements

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The absolute pressures of uranium and plutonium bearing species were measured by the effusion collection method, and were combined with the ion intensity determinations to yield the partial pressures at (O/M)₁ = 1.969.

$$\log p_{\text{UO}_2} \text{ (atm)} = (5.215 \pm 0.40) - (25,328 \pm 907)/T$$

$$\log p_{\text{UO}_3} \text{ (atm)} = (9.365 \pm 0.23) - (32,436 \pm 491)/T$$

$$\log p_{\text{PuO}_2} \text{ (atm)} = (7.460 \pm 0.49) - (31,034 \pm 1090)/T$$

$$\log p_{\text{PuO}} \text{ (atm)} = (6.042 \pm 0.13) - (27,212 \pm 279)/T.$$

The consistency of the thermodynamic data of the binary Pu-O and ternary U-Pu-O system is discussed. The standard free energy of formation of PuO₂ (g) has been recalculated to be $\Delta G_{f, \text{PuO}_2}(\text{g}) = -102,700 - 3.16 T$ kcal/mole.

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ABSTRACT

The evaporation behavior of the ternary oxide system ($U_{0.95}Pu_{0.05}O_{2-y}$ where $y=0$ to 0.06), has been studied between 1800 and $2300^\circ K$ by an effusion collection technique combined with mass spectrometric analysis of the vapor phase.

The general behavior of the system was analysed by following pressure and composition changes as a function of time. A quasi-congruently vaporizing composition was found at $(O/M)_s=1.97$ when following the change of composition in the solid at constant temperature starting at $(O/M)_s=1.94$ and 2.08 . The ion intensities of UO_3^+ , UO_2^+ , PuO_2^+ , and PuO^+ were measured as a function of both temperature and composition. The partial molar enthalpies of evaporation, $\Delta H(UO_3)=115.8$ kcal/mole, $\Delta H(UO_2)=148.4$ kcal/mole, $\Delta H(PuO_2)=141.9$ kcal/mole and $\Delta H(PuO)=124.5$ kcal/mole, were obtained from the least-squares equations of the $\log(I \cdot T)$ vs $1/T$ data at $(O/M)_s=1.969$.

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KEYWORDS

URANIUM OXIDES
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STOICHIOMETRY
VAPOR PRESSURE
HIGH TEMPERATURE
ENTHALPY
EFFUSION
EVAPORATION HEAT
FORMATION FREE ENERGY
CONSISTENCY
MASS SPECTROMETERS

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1. INTRODUCTION

The application of $(U, Pu)O_2$ solid solutions for fast breeder reactors requires high-temperature thermodynamic data from which reactions under operating conditions and changes in both O/M and U/Pu compositions can be predicted. The thermodynamic stability of the high-temperature phases is important since a change of composition will affect the physical properties and can lead to a phase transition with all its structural consequences, to changes in chemical activity and the chemical state of fission products, and to an enrichment of plutonium by fuel migration (1, 2), which would ultimately lead to changes in neutron flux and temperature gradient. High-temperature thermodynamic data are also of interest for high-temperature production processes, reprocessing and purification techniques.

Considerable attention has been paid to the evaporation behavior of both binary systems U-O (3-11) and Pu-O (12-16) although portions of their high temperature phase diagrams are still hypothetical. The U-O system exhibits an increase in the total pressure as the composition becomes superstoichiometric because of the rapid increase of UO_3 , and also an increase in the substoichiometric region because of the increase in the partial pressure of UO. A total pressure increase at higher temperatures, observed by Ackermann (4), is due to a decrease of the O/U ratio under vacuum, as shown by Ohse (7, 8), indicated by an increase of the lattice parameter which approaches 5.4714 \AA . A bivariant behavior was found for PuO_{2-x} in the high-temperature single phase region from O/M=2.0 to approximately 1.6 whereas a univariant behavior confirmed the two phase region in the range O/Pu=1.5 to 1.6. The vapor pressure was found to decrease from both phase boundaries of the single phase region towards a minimum at the congruently vaporizing composition. A slight shift of this minimum towards lower composition was predicted and observed with increasing temperature (13,14).

First attempts to understand the evaporation behavior of the ternary

system were made by Pascard (12) who measured the variation of the total pressure of uranium and plutonium bearing molecules over the solid solutions containing 10, 20 and 25 a/o Pu. Partial molar free energies of oxygen obtained from the EMF data of Markin and Rand (17) and free energies of formation from various evaporation studies of the binary systems were combined by Rand and Markin (18) to obtain calculated partial pressures as a function of composition in the ternary system. Since the electrochemical technique is limited in temperature by the use of solid electrolytes, extrapolations of several hundred degrees are involved in these calculations. To avoid errors direct measurements at high temperatures are to be preferred.

2. PREPARATION, PURITY AND ISOTOPIC COMPOSITION OF SAMPLES

To allow simultaneous alpha spectrometry of uranium and plutonium on the collection targets, 97.51 a/o enriched U-233 (containing 1.06 a/o U-234, 1.43 a/o U-238, and 43 ppm U-232) and 91.44 a/o Pu-239/7.79 a/o Pu-240 (containing 0.70 a/o Pu-241, 0.03 a/o Pu-242, 0.01 a/o Pu-238, and 0.03 a/o Am-241) were used for the substoichiometric range.

The ternary solid solutions were prepared by coprecipitation from a mixture of their nitrates and then calcined at 900 °C and reduced at about 600 °C. The powder was then pressed and sintered under hydrogen at 1600 °C (19). Before measurements were made the material was heat treated several hours at 2000 °K in vacuum. Average spectroscopic data are given in Table I.

3. MOLECULAR BEAM SOURCE AND EFFUSION COLLECTION TECHNIQUE

The samples were heated in tungsten-cells in an electron beam furnace (14). The experiments were carried out in an oilfree ultra high vacuum. Temperatures were measured with a micro optical pyrometer sighted into a black body hole drilled into the wall of the

Table I :Spectroscopic and chemical analysis of $(U_{0.85}Pu_{0.15})O_2$ samples .

Element	Conc. in ppm	Element	Conc. in ppm
B	1	Bi	< 1
Si	100	Al	10
Fe	200	Mo	< 3
Mg	50	Ca	< 100
Mn	< 1	Cu	20
Pb	< 1	Zn	< 50
Cr	< 5	W	< 10
Sn	< 1	Ta	200
Ni	< 4	Zr	< 100

tungsten effusion cells. A set of 8 windows was calibrated by a standard lamp inside the vacuum furnace to correct for the transmissivity of the interposed windows. The total furnace, including radiation shields and beam collimator, was mounted on an x-y micro table, thereby allowing its geometrical adjustment under vacuum and during heating. An optical system permitted geometrical adjustment, measurement of the cell-collimator distance with a cathetometer, and alignment of the cell orifice with the target holder or ion source of the mass spectrometer before, after, or during each measurement. The molecular beam intensity was monitored by the ion current while the total assembly was moved relative to the mass spectrometer, and when the maximum intensity was obtained, alignment was assured.

A UHV target collection apparatus, containing the quadrupole directly above the collection device, as shown schematically in Fig. 1, was designed to allow collection and mass analysis under exactly the same experimental conditions of sample composition, geometry and temperature. The ratios of the various ions could be determined before,

after or during each exposure by using perforated targets. To evaluate the target uranium and plutonium deposits by alpha spectrometry and total alpha counting, the specific activities and thus the isotopic compositions were chosen such that approximately equal activity peaks were obtained within the different pressure ratio ranges.

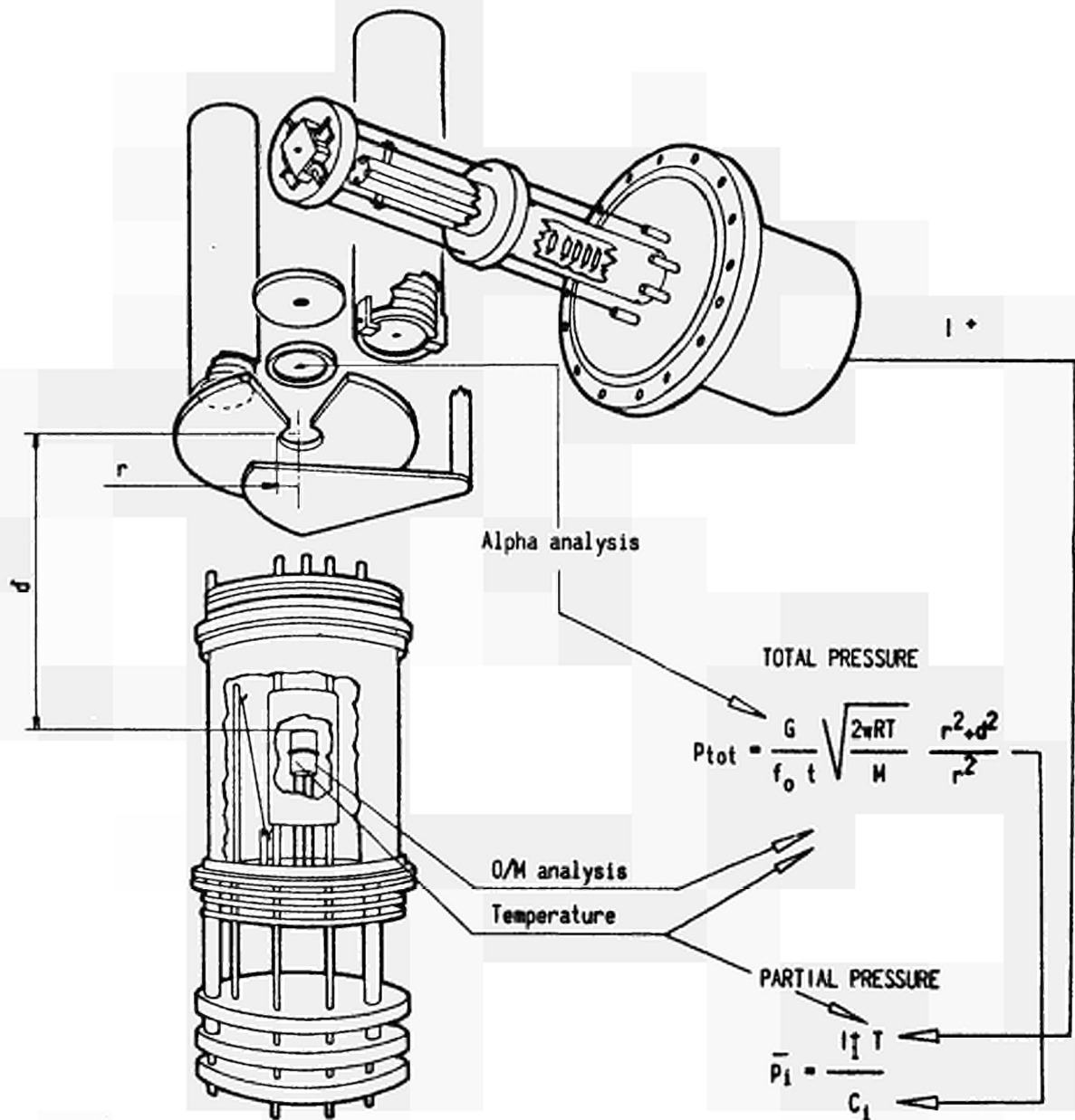


Fig. 1 : Determination of partial pressures by simultaneous application of the effusion collection technique and mass spectrometric analysis .

4. MASS SPECTROMETRIC ANALYSIS

An EAI mass spectrometer, Quad 250, was used to determine the relative abundance of PuO, PuO₂, UO₃ and UO₂ in the vapor over (U_{0.85}Pu_{0.15})O_{2-y} where y ranged from 0 to 0.06. To obtain relative ion intensities, corrections are necessary for ionization cross sections, electron energy differences, and multiplier efficiencies. The corrections for the ionization cross sections and the multiplier efficiencies were found (16) to compensate each other and are thus neglected.

Table II: Appearance and fragmentation potentials for UO₃⁺, UO₂⁺, PuO₂⁺, and PuO⁺.

Gaseous species		A P Energy in eV	F P	Ref.
UO ₃	UO ₃ ⁺	11.1 ± 0.4		10
	UO ₂ ⁺		13.6 ± 1	
	UO ⁺		22.5 ± 1.5	
UO ₂	UO ₂ ⁺	5.5 ± 0.4		10
	UO ⁺		13.6 ± 0.5	
PuO ₂	PuO ₂ ⁺	9.4 ± 0.5		16
	PuO ⁺			
PuO	PuO ⁺	5.8 ± 0.5		16

Because of the differences in appearance potentials of UO_3^+ , UO_2^+ , PuO_2^+ and PuO^+ , as given in Table II (10,16), intensity measurements were usually made at two or more electron energies. Various corrections for the electron energy differences are given in the literature. A normalization factor (6), obtained from the intensity ratio of one ion measured at two different energies, has been used to transform all ion intensities to one electron energy. In another method the same difference between the applied electron energy E and the appearance potential AP (16) is maintained equal for all species. Both methods are only reliable for energies below the first fragmentation potential and within the linear portion of the ionization efficiency curve. Since the first fragmentation potential of UO_3^+ to UO_2^+ (13.6 eV) is only 2.5 eV higher than the appearance potential of UO_3^+ (11.1 eV), the measurements of UO_2^+ and PuO^+ are difficult in the presence of UO_3^+ . These measurements can be made at a rather low electron energy in order to obtain equal (E-AP) potential differences. Otherwise fragmentation of UO_3^+ and UO_2^+ occurs which must be corrected for, and in this case the application of a normalization factor is not possible. The method of a direct calibration by means of the effusion collection technique, avoiding any fragmentation, was used in this study.

The direct calibration was achieved by combining the mass spectrometric measurements with the Knudsen effusion collection results, as schematically shown in Fig. 1. Within the total range of composition under investigation those compositions were chosen where the total pressure of uranium-or plutonium- bearing species is practically equal to the partial pressure of only one molecule. For UO_2 and PuO this condition is fulfilled near $\text{O}/\text{M} = 1.94$ where the ion ratios of $\text{UO}_2^+ / (\text{UO}^+ + \text{UO}_3^+)$ and $\text{PuO}^+ / (\text{PuO}_2^+ + \text{Pu}^+)$ are greater than 10/1. Assuming the total pressure of all uranium bearing species to be equal to the partial pressure of UO_2 , a specific ion sensitivity factor C_{UO_2} , including the instrument constant and all ion characteristics such as cross section, σ , and conversion factor K, can be determined according to

$$I_{\text{UO}_2}^+ \cdot T = p_{\text{UO}_2} \cdot A \cdot \sigma \cdot K \cdot V = p_{\text{UO}_2} \cdot C_{\text{UO}_2}$$

By measuring the ion current $I_{\text{UO}_2}^+$ and assuming the total pressure $p_{\text{tot}} = p(\text{UO}_2)$ at a given temperature T under constant experimental conditions, the factor C for UO_2 is obtained. Since the geometry can be kept constant, control of the conversion factor K and the multiplier gain V (by measuring mass 28) is sufficient.

With the ion sensitivity factor $C(\text{UO}_2)$ the absolute partial pressure of UO_2 can readily be calculated from the ion current at any other composition. This permits the determination of the partial pressure of UO_3 at a composition where both UO_3 and UO_2 are present. This can be done simply by subtracting the partial pressure of UO_2 from the measured total pressure of uranium bearing molecules at the same composition. This result in turn allows the calculation of $C(\text{UO}_3)$ from the intensity measurement. After all specific ion sensitivity factors have been determined by a repeated application of the above procedure, partial pressures can be determined at any composition by the measurement of ion currents.

5. GENERAL BEHAVIOR OF THE SYSTEM $(\text{U}_{0.85}\text{Pu}_{0.15})\text{O}_{2+y}$

Compared to the binary oxide systems Pu-O and U-O, where the minimum total pressure corresponds to a true congruently evaporating composition at $(\text{O}/\text{M})_s = (\text{O}/\text{M})_g$, both U/Pu and O/M ratios change continuously in the ternary mixed oxides. Thus a true congruently evaporating composition does not exist. Their quasi-equilibrium compositions $(\text{O}/\text{M})_s = (\text{O}/\text{M})_g$ and $(\text{U}/\text{Pu})_s = (\text{U}/\text{Pu})_g$ do not necessarily correspond to the minimum total pressure of the system. Because of the high oxygen potential in the mixed oxides and the mass dependent effusion rates, a quasi-congruently evaporating composition may be expected between the minimum total pressure and the composition at which $(\text{O}/\text{M})_s = (\text{O}/\text{M})_g$. The stability of this composition depends on the rate of change of $(\text{U}/\text{Pu})_s$. To verify these considerations isothermal heat treatments were carried out in open effusion cells with various super- and substoichiometric starting compositions. Fig. 2 shows the isothermal rate of composition change of the solid

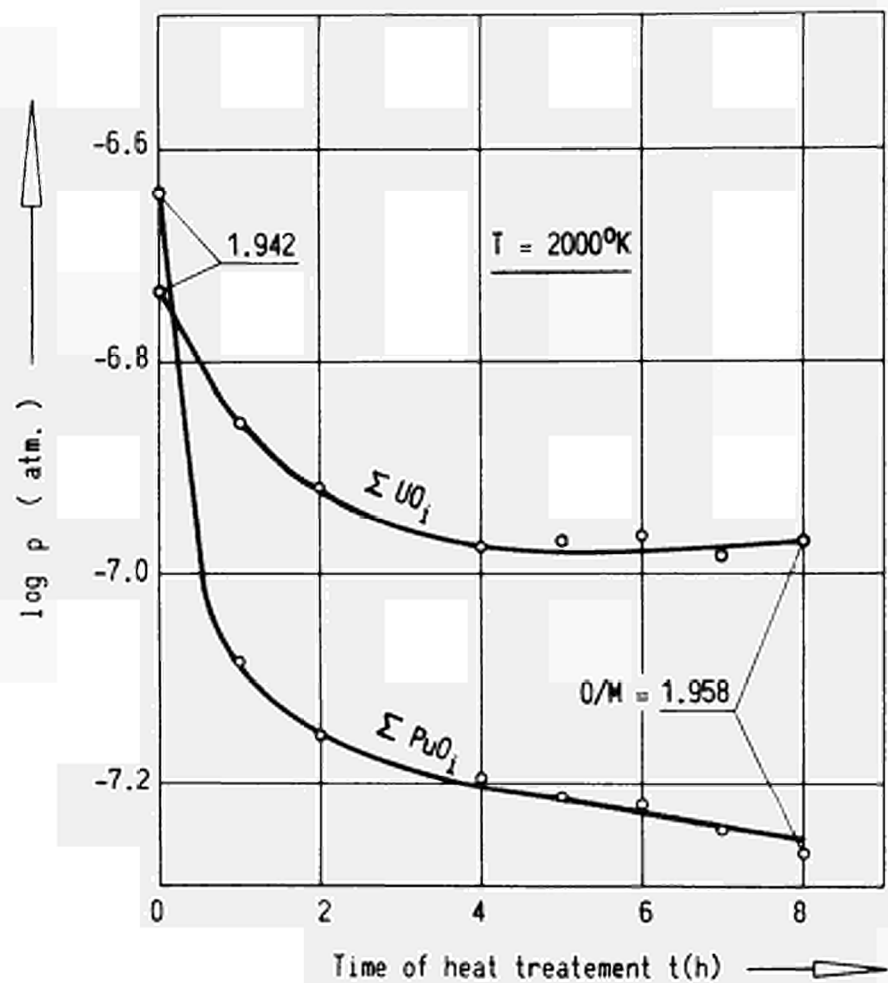


Fig 3 : Total vapor pressure of uranium and plutonium bearing gaseous species over $(U_{0.85}Pu_{0.15})O_{2-y}$ at constant temperature vs time .

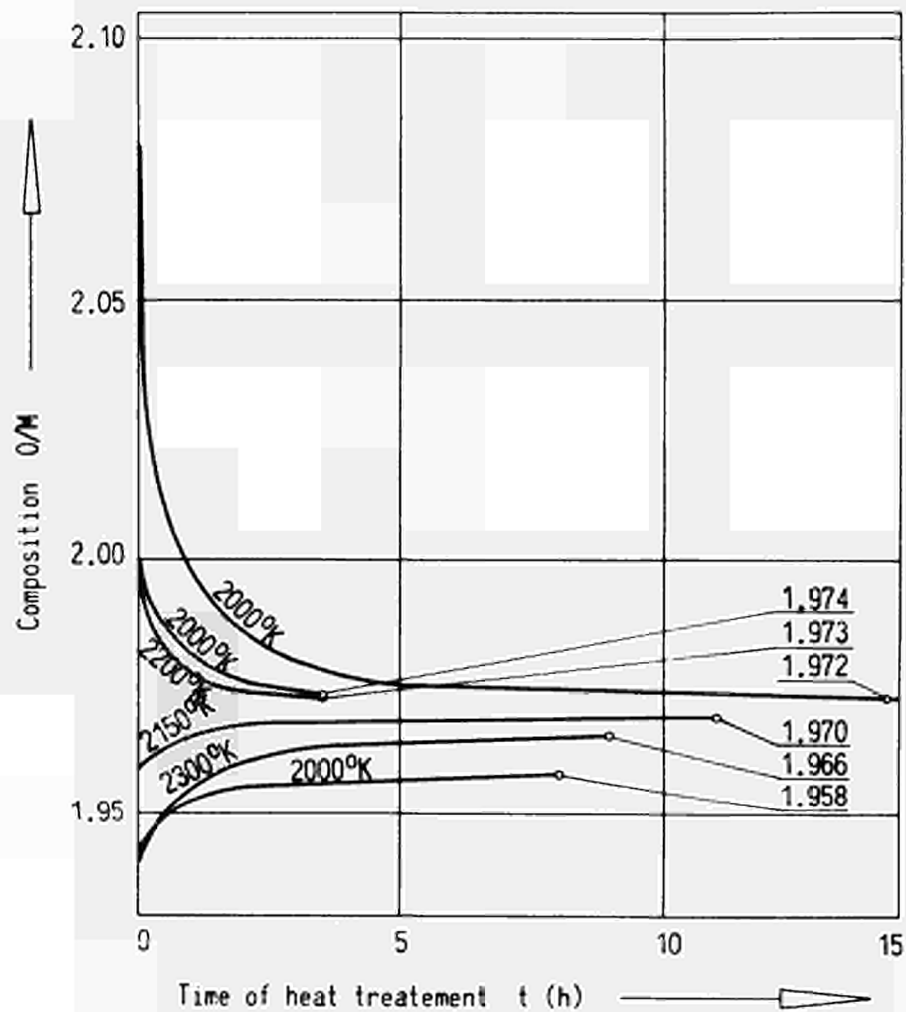


Fig 2 : Rate of change of composition O/M of $(U_{0.85}Pu_{0.15})O_{2\pm y}$ at constant temperature in UHV .

solution $(U_{0.85}Pu_{0.15})O_{2+y}$ as a function of time. A quasi-congruently evaporating composition near $(O/M)_s = 1.97$ is approached from both sides of the composition range. The rate of change increases, as one expects, with temperature and decreases as this quasi-congruently evaporating composition is approached (as $(O/M)_s$ approaches $(O/M)_g$) Fig. 3 shows the variation of the total pressure of all uranium and plutonium bearing gaseous species at 2000°K with a starting composition of 1.942. The plutonium pressure isotherm shows a considerably higher rate of change than does the pressure isotherm for the U containing total pressure. This indicates a rapid decrease of the partial pressure of PuO as shown in the binary system, and a comparatively slow decrease of UO_2 immediately compensated by the expected increase of UO_3 , which finally leads to a slight increase of the total uranium containing pressure.

6. TOTAL PRESSURE AND ION INTENSITY CALIBRATION

The total pressure of the uranium and plutonium bearing molecules was measured at both sides of the substoichiometric single-phase region of $(U_{0.85}Pu_{0.15})O_{2-y}$ in the composition ranges $(O/M)_s = 1.940$ to 1.952 and 1.992 to 2.00. The pressure is a function of both temperature and the composition variables O/M and U/Pu and therefore the system is trivariant. Within the time of temperature equilibration, and measurement times up to approximately an hour, changes in U/Pu can be neglected. Thus a bivariant behavior is actually observed. To avoid errors from changes in composition during heat treatment, all samples were quenched immediately after target exposure and analysed for O/M. Great care was taken to investigate possible composition gradients within the condensed phase. Measurements of O/M below 1.944 and above 1.996 were discarded because O/M ratio difference between the top and bottom part of the sample exceeded 0.003. Alignment and cosine distribution were checked by autoradiography and photometric analysis of the targets. The total pressures are given in Table III.

The various ion efficiency curves measured at low emission currents of 0.5 to 0.75 mA agreed fairly well with the appearance potentials and the first fragmentation potentials observed by other workers. Fragmentation of UO_2 was observed at 13.2. eV ($UO_2 = UO + O$) and the appearance potential

Table III: Total pressure of uranium and plutonium bearing gaseous species over ($U_{0.85} Pu_{0.15}$) O_{2-y} .

O/M ± 0.001	T (°K)	P (atm)		Log P (atm)	
		UO_x	PuO_x	UO_x	PuO_x
1.947	2075	$4.954 \cdot 10^{-7}$	$3.118 \cdot 10^{-7}$	- 6.305	- 6.506
1.950		$7.278 \cdot 10^{-7}$	$3.236 \cdot 10^{-7}$	- 6.138	- 6.490
1.952		$4.742 \cdot 10^{-7}$	$3.273 \cdot 10^{-7}$	- 6.324	- 6.485
1.992	2108	$2.266 \cdot 10^{-6}$	$1.173 \cdot 10^{-7}$	- 5.648	- 6.931
1.994		$2.409 \cdot 10^{-6}$	$1.087 \cdot 10^{-7}$	- 5.618	- 6.964
1.995		$2.635 \cdot 10^{-6}$	$1.047 \cdot 10^{-7}$	- 5.579	- 6.980

of UO^+ was found to be 5.7 eV. Therefore, an electron energy of 13 eV was chosen for all measurements, to avoid any fragmentation and yet provide a sufficiently high ion current for UO_3^+ which has the highest appearance potential of any of the ions in this system. Table IV gives the ion intensity calibration according to 4, containing the total pressure, ion intensities of PuO_2^+ , PuO^+ , UO_3^+ and UO_2^+ and the calculated ion sensitivity factors C_i .

7. ION INTENSITY MEASUREMENTS AND PARTIAL PRESSURES

Table V contains the ion intensities ($\log (I_i^+ \cdot T)$) and partial pressures ($\log p_i$), calculated from $\log p_i = \log (I_i^+ \cdot T) - \log C_i$. Fig. 4 gives the partial pressures versus the reciprocal temperatures at $\text{O}/\text{M} = 1.969$ in the temperature range from $T = 2000$ to 2350 °K. Table VI contains the least-squares equations for UO_3 , UO_2 , PuO_2 and PuO and second law partial enthalpy and entropy changes at this quasi-congruently evaporating composition of $\text{O}/\text{M} = 1.969$, assuming Δc_p to be negligible in the measured temperature range. Because of the rapid change of composition at both extremities of the substoichiometric single phase region (Fig. 2), $\log (I_i^+ \cdot T)$ or $\log p_i$ vs $1/T$ measurements cannot necessarily be interpreted as the partial enthalpy values, and therefore were not attempted.

The partial pressure-composition diagram presenting the various partial pressure isotherms for UO_3 , UO_2 , PuO_2 , PuO and O , as well as the total pressure at 2108 °K, is given in Fig. 5. The trivariant behavior of the mixed oxide system is mainly characterized by the rapid increase of the UO_3 partial pressure as the stoichiometric composition $(\text{O}/\text{M})_s = 2.00$ is approached and by the rapid decrease of PuO with increasing O/M . The total vapor pressure minimum around $(\text{O}/\text{M})_s = 1.97$ is rather flat and therefore not very well defined. The various ratios of $(\text{O}/\text{M})_g$ and $(\text{U}/\text{Pu})_g$ can be determined from the partial pressure-composition diagram in Fig. 5. The quasi-equilibrium $(\text{O}/\text{M})_g = (\text{O}/\text{M})_s$ occurs at $\text{O}/\text{M} = 1.964$, whereas $(\text{U}/\text{Pu})_g = (\text{U}/\text{Pu})_s$ at $(\text{O}/\text{M})_s = 1.968$. At the latter composition, the vapor is richer in oxygen than is the solid, and the composition of the solid will change toward a lower O/M ratio on continued vaporization.

Table IV : Ion sensitivity factors C_i determined by combining the total pressure from effusion measurements and the ion intensities from mass spectrometric analysis .

$(O/M)_s$	T (°K)	Ion intensity $I^+ \cdot T$ (amp deg K)	P tot. (atm)	Partial pressure P_i (atm)	C_i (amp deg K atm ⁻¹)	log C_i
1.944 1.947	2075 2075	$PuO^+ : 6.55 \cdot 10^{-7}$	$3.118 \cdot 10^{-7}$	$PuO : 3.118 \cdot 10^{-7}$	2.100	0.322
1.944 1.947	2075 2075	$UO_2^+ : 5.34 \cdot 10^{-7}$	$4.954 \cdot 10^{-7}$	$UO_2 : 4.954 \cdot 10^{-7}$	1.078	0.036
1.995 1.995	2108 2108	$PuO_2^+ : 3.76 \cdot 10^{-8}$	$1.047 \cdot 10^{-7}$	$PuO_2 : 0.947 \cdot 10^{-7}$	0.397	-0.401
1.995 1.995	2108 2108	$UO_3^+ : 1.97 \cdot 10^{-7}$	$2.635 \cdot 10^{-6}$	$UO_3 : 1.598 \cdot 10^{-6}$	0.123	-0.910

Table V: Ion intensities of PuO_2^+ , PuO^+ , UO_3^+ and UO_2^+ at an electron energy of 13 eV and partial pressure versus composition and temperature .

(O/M) _s	T °K	1/T (°K ⁻¹) 10 ⁻⁴	log I _i ⁺ .T (amp deg K)				log P _i (atm)			
			PuO_2^+	PuO^+	UO_3^+	UO_2^+	PuO_2	PuO	UO_3	UO_2
1.944	2075	4.819		-6.1838		-6.2725		-6.5058		-6.3085
1.969	2002	4.995		-7.2080		-6.7819		-7.5300		-6.8179
	2024	4.941		-7.0571		-6.6032		-7.3791		-6.6392
	2049	4.880		-6.9590		-6.4444		-7.2810		-6.4804
	2060	4.854		-6.8093		-6.2905		-7.1313		-6.3265
	2084	4.798		-6.6633		-6.1235		-6.9953		-6.1595
	2112	4.735		-6.5479		-5.9458		-6.8699		-5.9818
	2131	4.693	-7.4276	-6.4026	-7.5440	-6.0115	-7.0266	-6.7246	-6.6340	-6.0475
	2156	4.638		-6.2911		-5.6618		-6.6131		-5.6978
	2181	4.585	-7.2500	-6.1165	-7.3468	-5.4562	-6.8490	-6.4385	-6.4368	-5.4922
	2211	4.523	-7.0397	-5.9985	-7.1648	-5.3096	-6.6387	-6.3205	-6.2548	-5.3456
	2212	4.521	-6.9428	-5.9384	-7.0977	-5.2104	-6.5418	-6.2604	-6.1877	-5.2464
	2254	4.436	-6.7041	-5.7415	-6.9346	-4.9804	-7.3031	-6.0635	-6.0246	-5.0164
	2257	4.431	-6.7036	-5.6935	-6.9797	-4.9572	-6.3026	-6.0155	-6.0697	-4.9932
	2289	4.369	-6.4508	-5.4654	-6.7818	-4.7348	-6.0498	-5.7874	-5.8718	-4.7708
2322	4.307	-6.2984	-5.3196	-6.5416	-4.5618	-5.8974	-5.6416	-5.6316	-4.5978	
1.995	2108	4.744	-7.4248	-7.6778	-6.7055	-5.9508	-7.0238	-7.9998	-5.7955	-5.9868

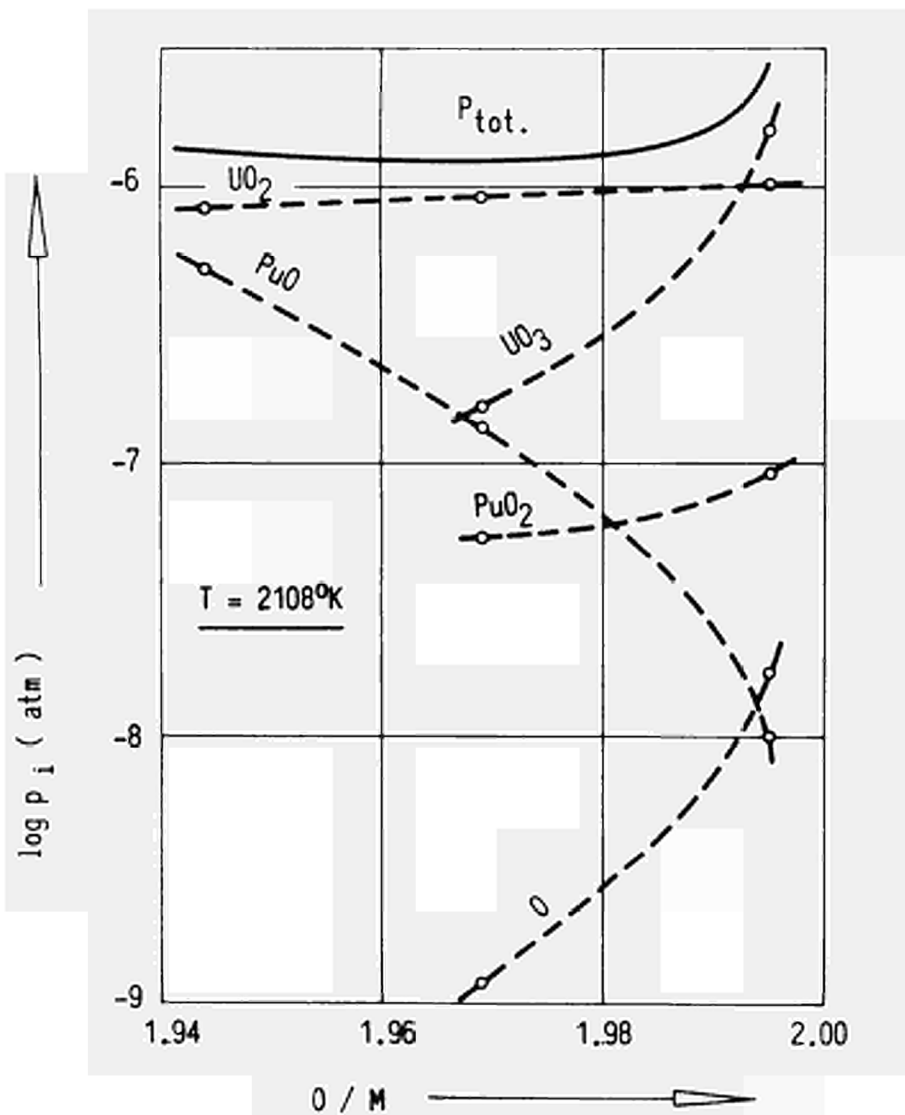


Fig. 5: Partial pressure - composition diagram of UO_3 , UO_2 , PuO_2 , PuO and O over $(\text{U}_{0.85}\text{Pu}_{0.15})\text{O}_{2-y}$ at $2108\text{ }^\circ\text{K}$.

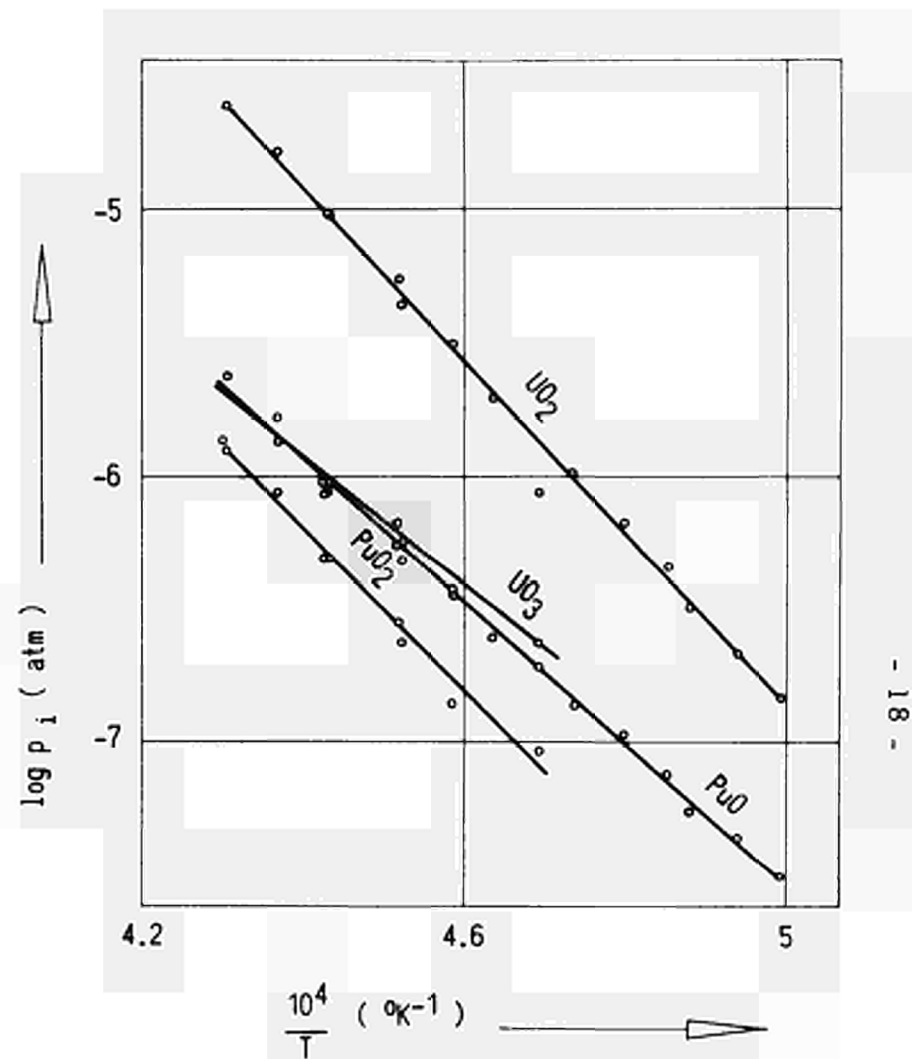


Fig. 4: Partial pressure of PuO_2 , PuO , UO_3 and UO_2 over $(\text{U}_{0.85}\text{Pu}_{0.15})\text{O}_{1.969}$ in the temperature range from $T = 2000\text{ }^\circ\text{K}$ to $2350\text{ }^\circ\text{K}$.

Table VI: Least square equations for partial pressures and second law partial enthalpies and entropies of evaporation for $O/M = 1.969$ and $T = 2000^{\circ}K$ to $2350^{\circ}K$.

$$\log P_{UO_3} \text{ (atm)} = (5.215 \pm 0.40) - (25328 \pm 907)/ T$$

$$\log P_{UO_2} \text{ (atm)} = (9.365 \pm 0.23) - (32436 \pm 491)/ T$$

$$\log P_{PuO_2} \text{ (atm)} = (7.460 \pm 0.49) - (31034 \pm 1090)/ T$$

$$\log P_{PuO} \text{ (atm)} = (6.042 \pm 0.13) - (27212 \pm 279)/ T$$

$$\Delta H (UO_3) = 115.8 \text{ Kcal/mole} \quad \Delta S (UO_3) = 23.86 \text{ e.u./mole}$$

$$\Delta H (UO_2) = 148.4 \text{ Kcal/mole} \quad \Delta S (UO_2) = 44.09 \text{ e.u./mole}$$

$$\Delta H (PuO_2) = 141.9 \text{ Kcal/mole} \quad \Delta S (PuO_2) = 34.13 \text{ e.u./mole}$$

$$\Delta H (PuO) = 124.5 \text{ Kcal/mole} \quad \Delta S (PuO) = 27.65 \text{ e.u./mole}$$

As a result of this change in the solid composition, however, the vapor will now contain more plutonium than the solid. Rand and Markin (18) have calculated that an initially stoichiometric 15 a/o plutonium solid solution will first lose oxygen and uranium preferentially, but that on continued vaporization the gas phase will change its composition until it is richer in plutonium and poorer in oxygen than the solid. At this point the solid must have an O/M ratio less than at the quasi-equilibrium $(O/M)_g = (O/M)_s$. They calculated that this situation will exist until all the plutonium is vaporized and solid $UO_{2.0}$ remains. Since our results agree well

with Rand and Markin's calculated pressures, these calculated trends are also probably correct.

8. CONSISTENCY OF THERMODYNAMIC DATA IN THE OXIDE SYSTEMS

The necessity of a recalculation of various thermodynamic data of the oxide systems has already been shown by vapor pressure data obtained in the binary oxide system Pu-O (12,14) and seems now generally accepted (20,21). The total pressure over $\text{PuO}_{1.92}$ ($\log p_e(\text{atm}) = 7.50 - 29,260/T$) given by Ackermann et al. (13) is below the pressure minimum of the congruently evaporating composition (near $\text{O/Pu} = 1.83$ to 1.87) found by Ohse and Ciani (14). This pressure dependency was used to calculate the partial pressure of PuO_2 at $(\text{O/M})_s = 1.92$ via the relationship $p_e = p_{\text{PuO}_2} + (271/255)^{1/2} \cdot p_{\text{PuO}}$, giving $\log p_{\text{PuO}_2}(\text{atm}) = 7.67 - 29,640/T$. Finally the standard free energy of formation of $\text{PuO}_2(\text{g})$ was calculated via the process $\text{PuO}_{1.92}(\text{s}) + 0.08 \text{O}(\text{g}) = \text{PuO}_2(\text{g})$ yielding $\Delta G_{f, \text{PuO}_2(\text{g})} = -113,100 + 4.35T$. The binary pressure data obtained from effusion measurements of Ohse and Ciani (14) give a partial pressure dependency of $\log p_{\text{PuO}_2}(\text{atm}) = 9.31 - 31,900/T$ at $(\text{O/Pu})_s = 1.92$. This yields a standard free energy of formation of $\Delta G_{f, \text{PuO}_2(\text{g})} = -102,700 - 3.16 T$. Using this value, the free energies given in Table VII and the partial pressure data of this study for $(\text{O/M})_s = 1.969$ in Table VI, very good agreement is obtained at 2108°K for the partial pressures of O_2 and O over the mixed oxides. Thus from the relation $\text{PuO}(\text{g}) + 1/2 \text{O}_2(\text{g}) = \text{PuO}_2(\text{g})$ a value $\log p_{\text{O}_2}(\text{atm}) = -12.17$ is obtained and from the equilibrium $\text{UO}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) = \text{UO}_3(\text{g})$ -12.18 is calculated. The corresponding values for the partial pressures of O are $\log p_{\text{O}}(\text{atm}) = -8.91$ for $\text{PuO}(\text{g}) + \text{O}(\text{g}) = \text{PuO}_2(\text{g})$ and -8.93 for $\text{UO}_2(\text{g}) + \text{O}(\text{g}) = \text{UO}_3(\text{g})$. This excellent agreement confirms the corrected value of $\Delta G_{f, \text{PuO}_2(\text{g})}$.

Table VII

Standard free energies of formation.

$$\Delta G_{f, \text{PuO}_2}^{\circ}(\text{g}) = - 102,700 - 3.16 T \quad (14)$$

$$\Delta G_{f, \text{PuO}}^{\circ}(\text{g}) = - 29,000 - 12.1 T \quad (13)$$

$$\Delta G_{f, \text{UO}_3}^{\circ}(\text{g}) = - 219,870 + 27.15 T \quad (22)$$

$$\Delta G_{f, \text{UO}_2}^{\circ}(\text{g}) = - 123,400 + 5.70 T \quad (3)$$

$$\Delta G_{f, \text{O}}^{\circ}(\text{g}) = 61,250 - 16.10 T \quad (23)$$

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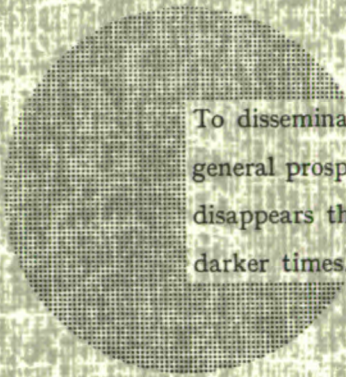
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