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DIFFUSION OF Pu IN UO<sub>2</sub>

by

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Joint Nuclear Research Centre  
Ispra Establishment (Italy)  
Chemistry Department

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The diffusion of  $^{239}Pu$  in sintered pellets of  $UO_2$  (density 10.6) has been measured with the methods of  $\alpha$  radiation absorption and sectioning. The temperature dependence of the diffusion coefficient is represented by the equation:  $D = 0.34 \exp(-97\,300 \pm 4\,100/RT) \text{ cm}^2 \text{ sec}^{-1}$ .

Comparison has been made with the self-diffusion of Uranium by a new technique of differential diffusion measurements. It results that the activation energy for Plutonium diffusion is 6.0 kcal less than that of Uranium diffusion.

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## Diffusion of Pu in UO<sub>2</sub>

By F. SCHMITZ and R. LINDNER, Chemistry Department, CCR Euratom Ispra (Italy) and Laboratory for Nuclear and Radiochemistry, Technical University Braunschweig (Germany)

With 3 figures. (Received May 10, 1963)

**Summary** The diffusion of <sup>239</sup>Pu in sintered pellets of UO<sub>2</sub> (density 10.6) has been measured with the methods of  $\alpha$  radiation absorption and sectioning. The temperature dependence of the diffusion coefficient is represented by the equation:  $D = 0.34 \exp(-97300 \pm 4100/RT) \text{ cm}^2 \text{ sec}^{-1}$ .

Comparison has been made with the self-diffusion of Uranium by a new technique of differential diffusion measurements. It results that the activation energy for Plutonium diffusion is 6.0 keals less than that of Uranium diffusion.

**Zusammenfassung** Die Diffusion von <sup>239</sup>Pu in UO<sub>2</sub>-Sinterkörpern (Dichte 10,6) wurde mit den Methoden der  $\alpha$ -Strahlenabsorption und der direkten Ermittlung der Konzentrationsverteilung untersucht. Die Temperaturabhängigkeit des Diffusionskoeffizienten wird durch die Gleichung  $D = 0,34 \exp(-97300 \pm 4100/RT) \text{ cm}^2 \text{ sec}^{-1}$  dargestellt.

Nach einem neuen Verfahren der differentiellen Diffusionsmessung ergab sich für die Diffusion des Plutoniums eine um 6,0 kcal kleinere Aktivierungsenergie als für die des Urans.

**Résumé** La diffusion du <sup>239</sup>Pu dans des comprimés frittés de UO<sub>2</sub> (de densité 10,6) a été mesurée par les méthodes d'absorption des rayons  $\alpha$  et des sectionnement. La dépendance du coefficient de diffusion se représente par l'équation  $D = 0,34 \exp(-97300 \pm 4100/RT) \text{ cm}^2 \text{ sec}^{-1}$ .

Par une nouvelle méthode différentielle de mesurer la diffusion une comparaison avec l'autodiffusion de l'uranium a été faite. Il en résulte que l'énergie d'activation pour la diffusion du plutonium est 6,0 kcal plus petite que celle de l'uranium.

### Introduction

The knowledge of cation diffusion in pure and mixed oxides and carbides, especially of Uranium and Plutonium is essential for the production<sup>1</sup>, homogenization and behaviour of these systems important for high temperature reactors and breeders.

After the measurement of Uranium diffusion<sup>2</sup> in UO<sub>2</sub> the diffusion of tracer quantities of <sup>239</sup>Pu is described.

<sup>1</sup> Cf. e. g. L. A. RUSSEL, N. H. BRETT, J. D. L. HARRISON and J. WILLIAMS, Observations on Phase Equilibria and Sintering Behaviour in the PuO<sub>2</sub>-UO<sub>2</sub> System, *J. Nucl. Mater.* **5**, 216 (1962).

<sup>2</sup> R. LINDNER und F. SCHMITZ, Diffusion von <sup>233</sup>U in Uran-dioxyd, *Z. Naturforsch.* **16a**, 1373 (1961).

**Methods**

Primarily the methods of alpha absorption and sectioning have been used as described in detail in an earlier publication<sup>2</sup>. In the case of the alpha absorption method the absorption function is measured in air and recalculated for UO<sub>2</sub>. The intensity vs range curve can be approximated by a straight line which facilitates the calculation. By appropriate choice of the relative position of source and detector<sup>2</sup> a "range" of the alpha radiation in UO<sub>2</sub> of 3.45 microns was obtained.

This sensitive and reliable method which permits to determine the time function of diffusion - as the specimen can be measured after various diffusion periods - has been checked in some cases with the sectioning method. This means that the sintered pellets which were planparallel from the beginning, were abraded on fine emery paper with a device described in a previous paper<sup>2</sup>. Cuts of about 0.5 microns were taken, the concentration gradient was found to have approximately the shape predicted for a homogeneous specimen.

Diffusion measurements on sintered bodies include a considerable limit of error. Similar diffusion values for Uranium and Plutonium are to be expected, and a method is required which allows an exact distinction between the relative diffusion values for the two elements. Use can be made of the different alpha energies of <sup>239</sup>Pu (5.15 MeV.) and <sup>233</sup>U (4.82 MeV.) in this connection. These two energies can easily be distinguished as peaks with a half-width of ca. 30 kcal. with a semiconductor detector and a multichannel pulse height analyzer. From a thin surface layer those two isotopes will diffuse into the interior of the specimen and consequently the surface concentration as indicated by the intensity of the alpha energy at its original value will decrease. The relative decrease of this intensity is a direct measure of the relative diffusion coefficient. This can be seen from the solution of the diffusion equation for distance zero:

$$C/C_0 = d/\sqrt{\pi Dt} \tag{1}$$

where  $C/C_0$  is the relative surface concentration,  $d$  the thickness of the initial layer,  $D$  the diffusion coefficient and  $t$  the diffusion time. From this equation results for the ratio of the diffusion coefficients:

$$\frac{D_{Pu}}{D_U} = \left[ \frac{(C/C_0)_U}{(C/C_0)_{Pu}} \right]^2 \tag{2}$$

This differential method does not necessitate the knowledge of thickness of the layer. The values obtained are independent from the variation of experimental parameters, as temperature control and heating time.

**Experiments**

Sintered pellets of pure UO<sub>2</sub> (furnished by the Aktiebolag Atomenergi Stockholm, Sweden) of an average density 10.6 g/cm<sup>3</sup>, diameter of 10 mm and height of 2 mm were used<sup>2</sup>. One face of the pellet was coated with the tracer isotopes by condensation from the

vapour phase upon evaporation of the tracer in carrierfree form from a tungsten ribbon<sup>3</sup>. The radioactivity of the thin layer was measured with an alpha radiation detector (cesium iodide plate and photo multiplier). The specimen was heated for diffusion in alumina vessels and alumina tubes in a stream of pure hydrogen. After the various diffusion periods the radioactivity was measured and from its apparent decrease the diffusion coefficient was calculated according to the equation derived in a previous paper<sup>2</sup>:

$$\frac{A}{A_0} = \operatorname{erf} \frac{R}{\sqrt{\pi Dt}} - \frac{2Dt}{R\sqrt{\pi Dt}} + \frac{2Dt}{R\sqrt{\pi Dt}} e^{-\frac{R^2}{4Dt}} [R = 3.45 \cdot 10^{-3} \text{ cm}]. \tag{3}$$

Generally the following approximation for  $A/A_0 > 0.75$  could be used:

$$\frac{A}{A_0} = 1 - \frac{2Dt}{R\sqrt{\pi Dt}} \rightarrow D = \frac{R^2 \pi}{4t} \left( 1 - \frac{A}{A_0} \right)^2 \tag{4}$$

**Results**

The results of the alpha absorption measurements at various temperatures are reproduced in Fig. 1. The values for the diffusion coefficient are reproduced in Fig. 2 as function of the inverse absolute temperature.

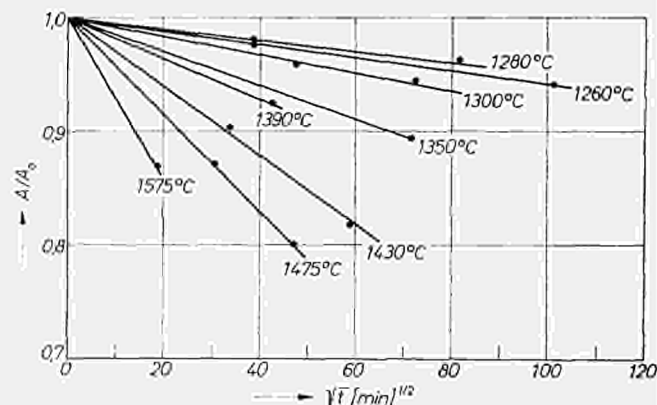


Fig. 1. Apparent surface  $\alpha$ -activity of <sup>239</sup>Pu coated UO<sub>2</sub> samples as function of diffusion time

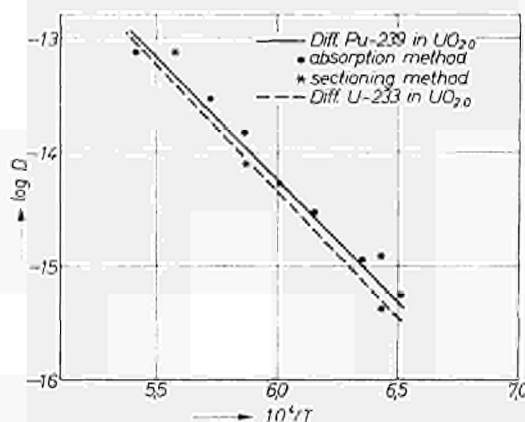


Fig. 2. Diffusion coefficients of Pu and U in UO<sub>2</sub> as function of temperature

<sup>3</sup> R. LINDNER and G. D. PARETT, Diffusion of Radioactive Magnesium in Magnesium Oxide, *J. Chem. Physics* **26**, 182 (1956).

The graph corresponds to:  $D = 0.34 \exp(-97.300 \pm 4.100/RT) \text{ cm}^2 \text{ sec}^{-1}$ . Fig. 2 contains as a dotted line the diffusion values for Uranium<sup>2</sup>. It seems that Plutonium diffuses slightly faster and has a smaller activation energy (97.3 vs 104.6 kcal/mole) than Uranium. Because of the limits of error (4 and 7 keals) a method of higher precision has to be used in order to confirm these findings.

The differential diffusion method as described above was used in experiments at 1250, 1350, 1443 and 1550°C respectively. The results are plotted in Fig. 3 in the form of  $\log(D_{\text{Pu}}/D_{\text{U}})$  vs  $1/T$ . As can be shown from the following equations, the slope of the straight line obtained is a direct measurement of the difference in activation energy of diffusion

$$\left. \begin{aligned} D_{\text{U}} &= D_{0(\text{U})} \exp - \frac{Q_{\text{U}}}{RT} \\ D_{\text{Pu}} &= D_{0(\text{Pu})} \exp - \frac{Q_{\text{Pu}}}{RT} \end{aligned} \right\} \quad (5)$$

$$\log \frac{D_{\text{Pu}}}{D_{\text{U}}} = \frac{\log e}{RT} (Q_{\text{U}} - Q_{\text{Pu}}) + \text{const}$$

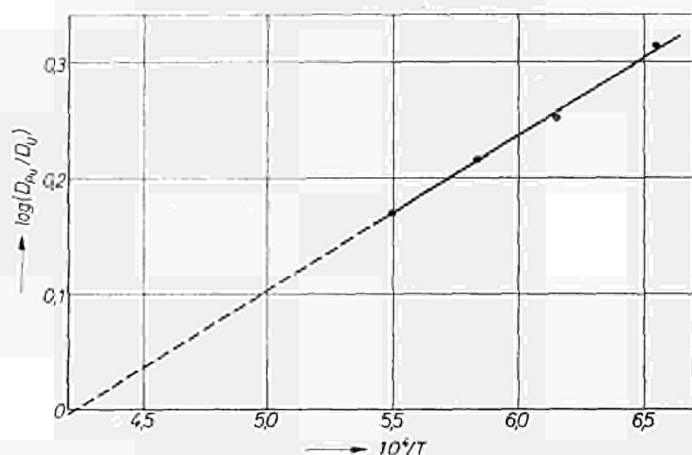


Fig. 3. Ratio of diffusion coefficients for Pu and U in  $\text{UO}_2$  as function of temperature

From the slope the difference of activation energy for diffusion is calculated to  $6.06 \pm 0.23 \text{ kcal mole}^{-1}$ .

(The same method was used for determining the ratio of diffusion coefficients for Am and Pu,  $^{241}\text{Am}$  being present in the  $^{239}\text{Pu}$  used as an impurity of about 3%. The activation energy for Am-diffusion was found to be 5.5 kcal./mole. higher than that for Pu-diffusion. This leads to  $Q_{\text{CO}_2}^{\text{Am}} = 102.2 \text{ kcal./mole.}$ )

### Discussion

1. It had to be expected that the  $\text{Pu}^{4+}$  ion with its smaller diameter (0.90 versus 0.93 Å) needs a smaller activation energy for diffusion than the  $\text{U}^{4+}$  ion. That has been confirmed by our experiments.
2. Our results confirm the diffusion values previously obtained for Uranium<sup>2</sup>. These are somewhat deviating from those ( $88 \pm 11 \text{ kcal mole}^{-1}$ ) obtained by other authors<sup>4</sup>.

Usually the highest activation energies are the most trustworthy ones. For a comparison of the results obtained by different authors a detailed knowledge ought to be available of the physical state, the chemical composition and the gas atmosphere surrounding the diffusion sample. A minor influence of impurities as e.g. introduced into the sample by the coating process cannot be excluded.

We plan to continue experiments of this kind with other high-melting systems as pure and mixed carbides of Uranium and Plutonium as well as of Uranium and Thorium.

We acknowledge the efficient support by Drs. F. CAPELLANI and G. RESTELLI in the measurement of the alpha spectra.

<sup>4</sup> A. B. AUSKERN and J. BELLE, Self Diffusion in  $\text{UO}_2$ , J. Nucl. Mat. **3**, 311 (1961).





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