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European Institute for Transuranium Elements, EURATOM
D-7500 Karlsruhe, Postfach 2266, FRG

Résumé. — La diffusion de U-233 et de Th-228 a été étudiée dans des échantillons monocristallins et polycristallins entre 1 400 et 2 200 °C. Dans ce domaine, la diffusion intergranulaire est en majorité dans les échantillons frittés. Dans les monocristaux il faut faire très attention, et les profils de concentration ainsi que la dépendance du temps de pénétration des radio-traceurs doivent être mesurés afin d'éviter des résultats erronés (artefacts dus au relâchement en surface). Il est montré que la plupart des références induisent en erreur car les coefficients de diffusion rapportés sont beaucoup trop grands et les enthalpies d'activation beaucoup trop petites. La véritable énergie d'activation est $\Delta H \sim 6,5$ eV/atome (150 kcal/mole) et les vrais coefficients de diffusion $D \sim 10^{-18}$ cm² s⁻¹ à 1 600 °C.

Abstract. — The diffusion of U-233 and Th-228 was studied in ThO₂ single-crystals and sinters between 1 400 and 2 200 °C. In this temperature range, grain boundary diffusion dominates in polycrystals. In single crystals, great care has to be taken and both the depth and the time-dependence of tracer penetration should be measured in order to avoid erroneous results (artifacts, as e. g. due to surface relaxation). It is shown that most literature data are misleading since the reported diffusion coefficients are much too high and the activation enthalpies are much too low. The true activation energy is high with $\Delta H \sim 6.5$ eV/atom (150 kcal/mole) and the true diffusion coefficients are low with $D \sim 10^{-18}$ cm² s⁻¹ at 1 600 °C.

1. Introduction.

In the materials of the fluorite structure, both in the earth alkaline fluorides CaF_2 and BaF_2, as well as in the oxides ThO_2, UO_2, $(U, Pu) O_2$ etc., the metal atoms diffuse at a much smaller rate than the non-metal atoms. The latter will therefore be rate-controlling for any diffusion-controlled high temperature kinetic process. Results on the diffusion of Th and U in ThO_2 have been reported by various authors [1-6], showing, however, an unusually big scatter. King [5] suggested that most of these data might be influenced by grain boundary or dislocation diffusion, and that volume diffusion proceeds at much lower rates than previously thought. In the present study, very extensive diffusion anneals using both sinters and single crystals were performed in a broad temperature range. Also, care was taken to follow the time dependence of tracer penetration at constant temperature to get an additional means to separate volume diffusion from disturbing other phenomena. The results give the final proof for slow metal atom diffusion in ThO_2.

2. Experimental.

The specimens used in this study were both polycrystals and single crystals. The ThO_2 sinters had a grain size of about 25 µm and metallic impurities of ~ 250 ppm. The single crystals were cut from arc-fused lumps supplied by the Norton Co. and were from the same batch as those used by King [5]. As in his samples, the main impurities were Fe, Al and Si in the 20 to 40 ppm range. The crystals contained some porosity and had a few cracks.

All samples were polished to a mirror-like flat surface by abrading on successively finer grades of diamond paste and by lapping. Following a preannealing treatment, the polished surfaces were coated with a thin (U-233) O_2 tracer layer by flash evaporation from a W-ribbon, or Th-228 atoms were bombarded into the specimens using a U-232 recoil source. The samples were annealed as sandwiches between 1 400 and 2 200 °C in vacuo for up to 140 h. At different times during the anneal, the penetration profiles of the tracer were measured by high resolution α-spectroscopy without destroying the samples. For this purpose, the α-energy degradation method of Schmitz and Lindner [7, 8] and measured values [9] of the energy loss of α-particles in ThO_2 were used.

3. Results.

A first set of experiments was performed at 1 430 °C. Figure 1 shows a plot of the mean tracer penetration, $\sqrt{4 Dt}$ in µm, versus the square root of the annealing time. The slope of such a plot yields the diffusion coefficient, D. A first fast initial tracer penetration, in previous measurements [10] on UO_2 explained as being due to *surface smoothening* or *accomodation of the tracer layer to the surface*, was followed by a hardly noticeable slope for single crystals and an apparent slope for
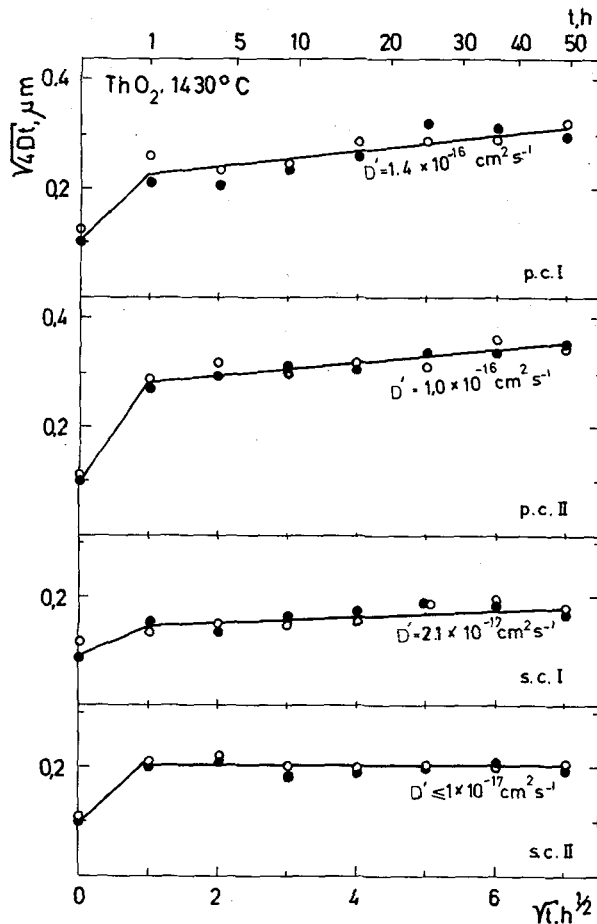
FIG. 1. — Experiments on the diffusion of U-233 in ThO₂ sinters (p. c.) and single crystals (s. c.). Some initial tracer penetration simulates diffusion.
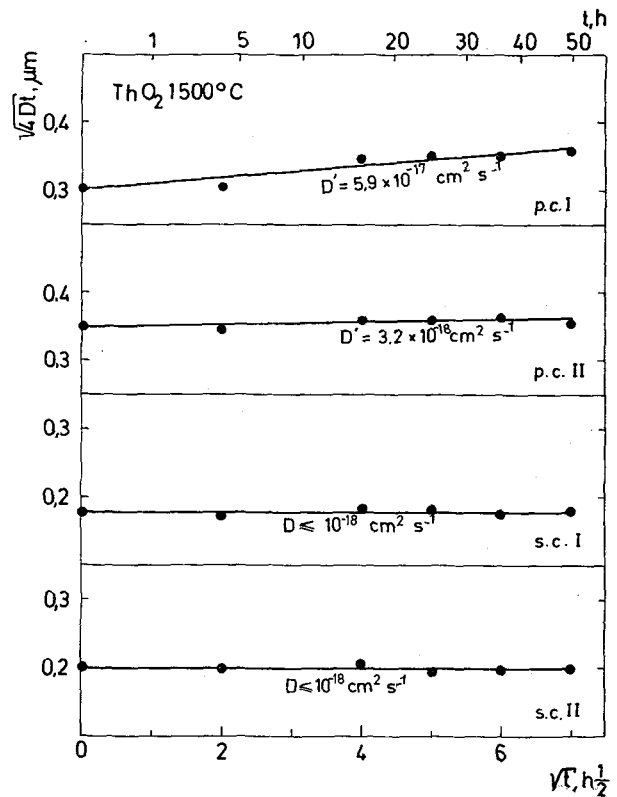

FIG. 2. — Experiments on the diffusion of U-233 in ThO₂ sinters (p. c.) and single crystals (s. c.). The anneal at 1 500 °C, subsequent to that at 1 430 °C (fig. 1), shows the absence of measurable diffusion.

sinters. The calculated apparent diffusion coefficients are given along the experimental curves. On further annealing the same samples at 1 500 °C, no further noticeable tracer penetration is observed for the single crystals yielding an upper limit for the diffusion coefficients D of 1×10^{-18} cm² s⁻¹. The sinters still indicate some tracer penetration. At higher temperatures, diffusion in the single crystals becomes measurable (Fig. 3). Both time and depth dependence indicate volume diffusion. The D-values are still very low and are, in fact, below the detection limit of conventional sectioning techniques though they are easily measurable with the present high resolution α-energy degradation technique [7, 8].

A more careful analysis of tracer penetration in ThO₂ sinters shows that in polycrystalline ThO₂, grain boundary penetration dominates. This is true for all experiments performed up to 2 000 °C. Whereas tracer penetration in volume diffusion gives Gaussian penetration profiles and a $\sqrt{t}$ dependence according to
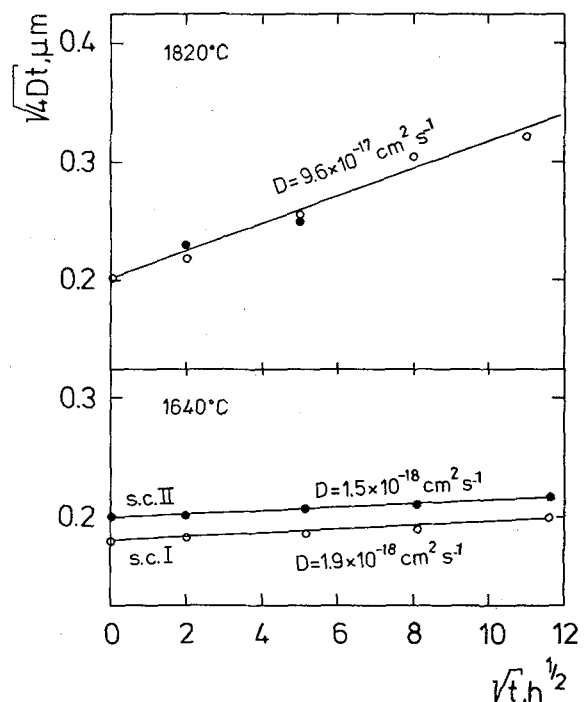
$$c(x, t) = c_0(\pi Dt)^{-1/2} \exp(- x^2/4\ Dt)$$

FIG. 3. — Diffusion of U-233 in ThO₂ single crystals at 1 640 and 1 820 °C.

grain boundary diffusion is known to yield straight lines in the penetration plots of log c versus x (or $x^{6/5}$) and to proceed with $\sqrt[4]{t}$. Here $c(x, t)$ = tracer concentration at depth x on annealing for time t and c_0 = concentration of instantaneous tracer source at $t = 0$, $x = 0$. Figure 4 indicates that a $\sqrt[4]{t}$-law (upper part) gives a better fit for tracer penetration in sinters than a $\sqrt{t}$ law (lower part), and figure 5 shows that a simple x-law covers most of the tracer penetration in ThO$_2$ sinters.
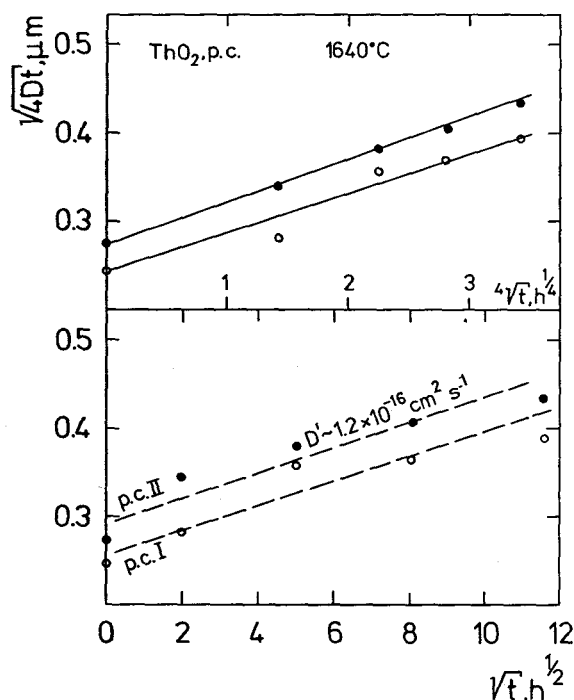

FIG. 4. — Diffusion of U-233 in ThO$_2$ sinters at 1 640 °C. In the upper part, a better fit is obtained indicating predominant grain boundary diffusion.
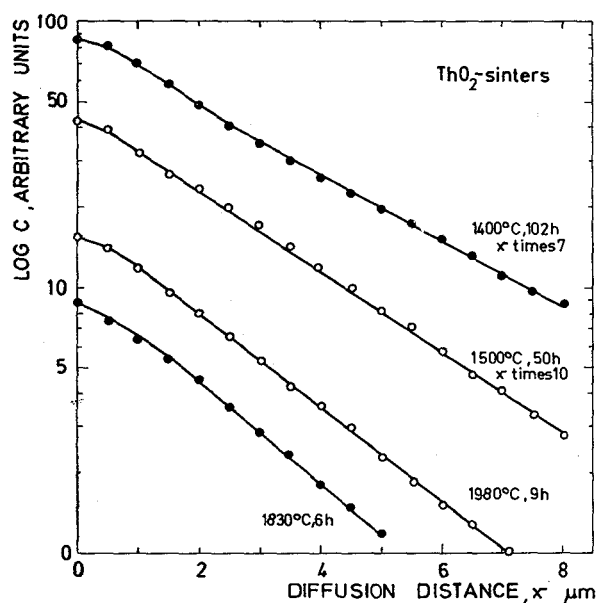

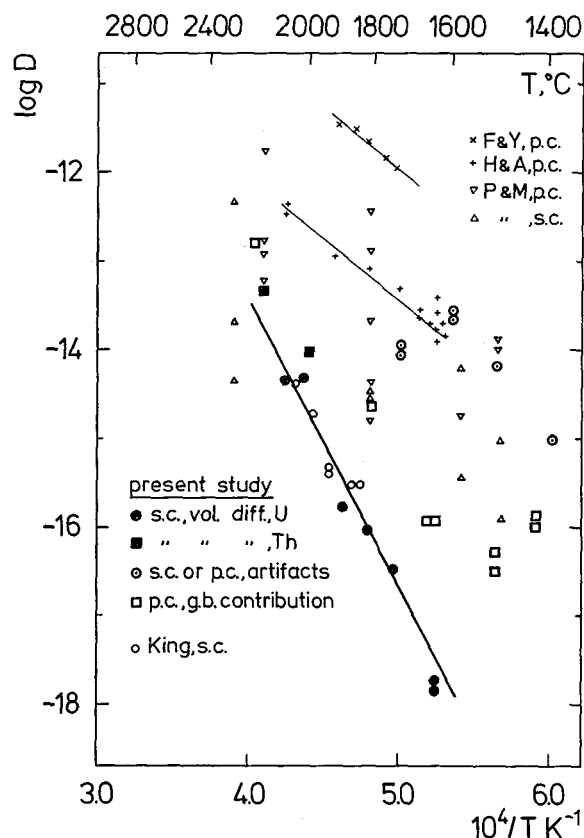FIG. 5. — Penetration curves for U-233 in ThO$_2$ sinters.

FIG. 6. — Arrhenius diagram for the diffusion of U and Th in ThO$_2$ giving the present results with those of Furuya and Yajima [1, 2], Hawkins and Alcock [3], Poteat and Morgan [4], and King [5].

Figure 6 finally summarizes the present data and compares them to the published literature results [1-5]. By using long annealing times and single crystals, tracer penetrations compatible with volume diffusion kinetics were obtained. These diffusion coefficients are given as full circles (for U-233) and full squares (Th-228). The temperature dependence of the data for U-233 can be described by

$$D = 0.5 \exp(- 150.000/RT) \text{ cm}^2 \text{ s}^{-1}.$$

Sinters of ThO$_2$ show always kinetics indicating predominant grain boundary diffusion. If nevertheless the penetration curves are (wrongly) evaluated as if due to volume diffusion, results as those shown by the open squares are obtained. Such an evaluation is meaningless, but the obtained figures tend towards the reported literature data. If finally the first fast surface relaxation effect is not corrected for [10], any result can be obtained depending on the annealing time used. Such results are artifacts and some are given in figure 6 as open circles with a dot. These fall into the scatter band of reported literature data.

4. **Discussion.** — The present results show that metal atom diffusion in ThO$_2$ is much slower than previously thought. Using long annealing times,

single crystals and a technique allowing to follow *both* the depth and time dependence of tracer penetration, reliable results are obtained. These indicate also a much higher activation enthalpy for diffusion ($\Delta H = 150$ kcal/mole or 6.5 eV/atom) than most previous studies. Only the data of King [5] can thus be considered to be representative.

A possible criticism of the present data could be based on the model of the defect structure of fluorite type materials published earlier [11]. This model explained the measured dependence of U and Pu diffusion in $UO_{2\pm x}$ and $(U, Pu) O_{2\pm x}$ on deviations from stoichiometry by postulating for metal atom diffusion

— a vacancy mechanism for MO_{2+x} with a low activation energy of $\Delta G_S - 2 \Delta G_{FO} + \Delta H^m_{M,v}$,

— a vacancy mechanism also for stoichiometric MO_2 with a higher activation energy

$$\Delta G_S - \Delta G_{FO} + \Delta H^m_{M,v},$$

— a minimum in diffusion for MO_{2-x} with a maximum in activation energy which changes whenever the diffusion mechanism changes from vacancy to interstitial, hence

$$\Delta G_S + \Delta H^m_{M,v} \quad \text{or} \quad \Delta G_{FM} - \Delta G_S + \Delta H^m_{M,i}$$

where ΔG = free energy of formation of
        S = Schottky defects
        FO = oxygen Frenkel defects
        FM = metal Frenkel defects
and ΔH^m = migration energy for
        M = metal (U or Pu)
        v = vacancy
        i = interstitial.

Later work [12-14] has confirmed the minimum in D and the maximum in ΔH for $(U, Pu) O_{2\pm x}$. In this material which is isostructural with ThO_2, deviations from stoichiometry are easily achieved by changes in the oxygen partial pressure during annealing since U^{4+} can easily be oxidized to U^{5+} or U^{6+}, and Pu^{4+} can be reduced to Pu^{3+}. In contrast, ThO_2 is much more stable. However, one might argue that the model holds for ThO_2 as well and that a slight reduction might have occurred [†], or that some trivalent impurity might have simulated a reduced state. This possibility, however, is thought to be unlikely because of three reasons

— the present data agree with those of King [5] though be used an argon annealing atmosphere whereas in the present work high vacuum was used. Furthermore, anneals in air at 1 500 °C gave similar small D-values as anneals in vacuum ;
— the previous higher data can be shown to coincide with artifacts or short-circuit phenomena ;
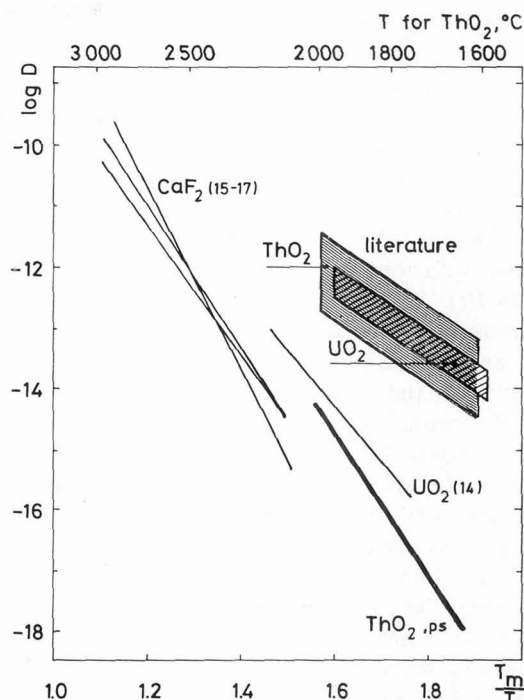— the present data agree well with reliable results for the remaining materials of the fluorite structure.

FIG. 7. — Normalized Arrhenius diagram comparing the present data for ThO_2 with reliable results of cation diffusion in other materials of the fluorite structure. The two dashed areas show previous data which are now rejected.

This latter argument is verified in figure 7 in form of a normalized Arrhenius diagram (log D versus T_m/T rather than $1/T$, with T_m = melting point in K). The rejected literature data are indicated by scatter bands for ThO_2 and UO_2. These UO_2 data have already previously been critizised [10]. If artifacts and short-circuit phenomena are minimized or avoided, all data available for fluorite structure materials show similar behaviour, both ThO_2 and UO_2 [13, 14] as well as CaF_2 [15-17]. This implies that diffusion below about 0.5 T_m in all materials is negligeably small. Much of the previous work on ThO_2 and UO_2 was done near 0.5 T_m.

The present study shows also that no reliable information on volume diffusion can be obtained with ThO_2 sinters (grain size $\sim$ 25 μm) below 2 000 °C. Both time (Fig. 4) and depth dependence (Fig. 5) of tracer penetration indicated that most of the tracer penetration was due to grain boundary diffusion. Though it was not the purpose of the present study to investigate grain boundary diffusion in ThO_2, the results indicate that grain boundary diffusion coefficients, D_{gb}, are of the order of 10^{-7} to 10^{-6} cm^2 s^{-1} at 2 000 °C and 10^{-10} to 10^{-9} cm^2 s^{-1} at 1 400 to 1 500 °C. The resulting activation enthalpy, though being very uncertain, fits the conventional relation (e. g. [18])

$$0.5 \, \Delta H_{vol} < \Delta H_{gb} < 0.8 \, \Delta H_{vol}$$

and is therefore similar to ΔH's previously reported for volume diffusion. Note also, that if published volume diffusion coefficients D are rejected, the

D_{gb}-values reported in the same publications must be rejected (or corrected) as well since the experimentally measured quantity is always the ratio D_{gb}/D.

In addition, the present study shows that the initial fast tracer accomodation that was reported for UO_2 before [10], occurs also with ThO_2. As e. g. indicated in figure 1, this phenomenon causes a tracer penetration of about 0.1 to 0.2 μm which, if taken as due to volume diffusion and as representing some quantity like $(4\,Dt)^{1/2}$, can yield any D-value depending on the annealing time chosen. This phenomenon represents an artifact and is most probably due to a fast relaxation of the surface to an equilibrium state [10, 19] possibly caused by anisotropies in surface energy and a surface diffusion or evaporation-condensation process. The effect was shown to depend on surface roughness [10] but is probably not affected by the tracer layer since it was observed for recoil bombardment with Th-228 atoms as well. For proper correction, the time dependence of tracer penetration must be investigated. This has never been done before and would be very time-consuming if sectioning was to be applied to measure diffusion profiles.

It is suggested that much of the previous literature has suffered from either this effect and/or from short circuit phenomena. Some of the literature (e. g. [3]) reported a high tracer concentration at the surface which was neglected as a bound surface layer. Most probably this part of the tracer constituted the contribution of volume diffusion to the penetration profile. Due to the surface smoothening effect and also because of the relatively high vapour pressures of the fluorite-type oxides, the existence of a bound surface layer is extremely unlikely. Rather, the danger exists, that diffusional effects are simulated by mass transfer due to evaporation-condensation (see ref. [12] for the case of UO_2 and $(U, Pu) O_2$). In fact, oxide samples annealed in vacuum can easily show a tracer transfer and embedding from one specimen to the other of the diffusion sandwich if only a very minute temperature gradient — a few °C are sufficient — exists between the two specimens.

Compared with the effects of non-volume diffusional contributions to tracer penetration, the differences in mobility between Th and U are small. It would be premature to speculate on the indicated difference, in particular since two different techniques, flash evaporation for U and recoil bombardment for Th, were used to label the specimens with the tracer.

5. **Conclusions and summary.** — The present study shows :

— that volume diffusion of uranium and thorium in ThO_2 is much slower than most published literature predicts ($D \sim 10^{-18}$ cm^2 s^{-1} at 1 600 °C) ;

— the true activation enthalpy ΔH is much higher than most reported values ($\Delta H \sim 6.5$ eV/atom) ;

— most literature values are affected by artifacts and/or short circuit phenomena ;

— grain boundary diffusion dominates in normal ThO_2 sinters to such an extent that volume diffusion cannot be measured reliably even at 2 000 °C ;

— a good correlation exists between cation diffusion and melting point in the materials of the fluorite structure investigated so far.

These results are of importance for both new and old reports on kinetic high temperature processes in ThO_2 as sintering, creep, grain growth etc. Whenever a rate-determining mechanism was suggested on basis of numerical agreement with the reported values of the diffusion activation enthalpy, a reinterpretation is necessary. The present work indicates that ΔH_{gb} rather than ΔH_{vol} is compatible with the earlier ΔH's-values.

† *Note added in proof* : Recent work has shown that ThO_2 turns black at high temperatures indicating some reduction. At 2 200 °C and prolonged annealing, a very small (recoverable) weight loss was noted. Yet, it is unlikely that any of the conclusions were affected since the reductions occurred only at the highest temperatures and their degree was very small.

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DISCUSSION

C. R. A. CATLOW. — I was pleased to see that you measured higher Arrhenius energies for cation diffusion in UO_2. This brings the experimental data into much closer agreement with the results of my own theoretical studies.

Hj. MATZKE. — This is inded the case.