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Publication Date
1983-05-01
Materials & Molecular Research Division

To be submitted for publication

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May 1983

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098
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TRACER SURFACE DIFFUSION ON UO₂

by

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ABSTRACT

Surface diffusion on UO$_2$ was measured by the spreading of U-234 tracer on the surface of a duplex diffusion couple consisting of wafers of depleted and enriched UO$_2$ joined by a bond of uranium metal. Spurious gas phase transport was eliminated by a masking technique. Surface diffusion coefficients measured at temperature between 1760 and 2110°C ranged from 0.1 to 2 cm$^2$/s. These results correspond to Arrhenius-type behavior with an activation energy of 72 ± 15 kcal/mole and a preexponential factor 5 x 10$^6$ cm$^2$/s with a 1-2 order of magnitudes uncertainty range. The preexponential factor was in reasonable accord with the nonlocalized surface diffusion model of Bonzel, although the jump distance implicit in this theory appears to be unacceptably large. No significant effect of the atomic weight of the inert species in the gaseous environment at 1 atm pressure was detected, a result which is not inconsistent with the theory.
INTRODUCTION

Mass transport methods such as scratch decay and grain boundary grooving are responsible for nearly all of the data on surface self diffusion on UO$_2$ (1-5). The data obtained by Marlowe and Kaznoff (6) using a tracer technique have been claimed to be in good agreement with the results of mass transport experiments (4,5). However, Robertson (7) first pointed out that correct interpretation of the data of Marlowe and Kaznoff to account for simultaneous volume and surface diffusion during tracer spreading results in much larger surface diffusivities than originally reported by these authors. Each improvement in the mathematical treatment of the tracer spreading problem (8, 9, 10) resulted in larger deduced values of surface diffusivity, until now the discrepancy between the mass transport and tracer results at 1900°C stands between three and four orders of magnitude. Although the surface diffusion coefficients from several different mass transport experiments are quite consistent, Matzke (11) was unable to perform such an experiment on single crystal specimens because of the development of striations on the surface which grew rather than diminished with annealing time.

Surface mobility may not be a unique property of the solid. The possibility that surface diffusion on UO$_2$ might depend upon collision between UO$_2$ molecules migrating on the surface and atoms impinging from the gas phase has been suggested independently by Buescher and Meyer (12) and by Mikhlin (13). This notion has been further developed by Nixon and MacInnes (14). Variation of the gaseous atmosphere during the diffusion anneal may help elucidate this feature of the process.
For accurate results, a tracer surface diffusion experiment should incorporate the following features.

- A masking technique to protect the surfaces from evaporation or spurious transport of tracer by molecular diffusion in the gas. The later parasitic transport process was shown to be very significant in the work of Furuya and Koizumi (15).

- A simple geometry of the diffusion couple to permit accurate analysis of the data to yield the surface diffusion coefficient.

- A method of reducing the solid-solid contact resistance between enriched and depleted parts of the diffusion couple.

- Avoidance of pure hydrogen or strongly oxidizing gases in contact with the solid during the anneal. Such environments can alter the oxide stoichiometry and thereby affect the uranium volume diffusion coefficient on which data interpretation depends.

- Use of isotopically enriched and depleted uranium in the oxide diffusion couple, with U-234 as the actual tracer. Use of plutonium as a "chemical tracer", as in the experiments of Furuya and Kozumi (15), risks gas transfer of the heavy metals between the source and sink components of the couple, as has been demonstrated by Matzke and Lambert (16).

The diffusion couple consisted of two wafers of UO₂, one of which was enriched to 93% U-235 and the other depleted to 0.2% U-235. The two wafers were bonded together so that surface exchange of uranium isotopes across the wafer-wafer interface was reasonably efficient. Isotope exchange across the interior portion of the interface by volume diffusion also occurred, but very slowly compared to exchange by surface
diffusion. When heated, uranium isotopes transferred between the two wafers but no net uranium flow took place. The face of the enriched wafer lost the light isotopes by volume diffusional exchange with U-238 supplied by the depleted wafer. The reverse process occurred on the face of the depleted wafer. Transport of the uranium isotope was along the surface, but storage of the tracer in quantities sufficient to measure by detection of the alpha particles emitted by U-234 required diffusion into the solid from the surfaces. Even though an interface resistance arising from imperfect joining of the two wafers was present, the symmetry of the duplex specimen streamlined the mathematical analysis of the coupled surface and volume diffusion model of tracer spreading. These processes led to radial distribution of the alpha radioactivity along both faces of the specimen following an anneal. Because the bulk of the initially depleted wafer contained little U-234, radial spreading of the tracer was most accurately determined by measurement of this face. The comparable reduction in tracer concentration in the enriched wafer was difficult to detect because of the high background radioactivity from the bulk of this material.

EXPERIMENTAL

Each UO₂ wafer was 1 mm thick and 15 mm in diameter. The enriched and depleted wafers were sintered together with the aid of a thin uranium metal foil placed between them. Annealing at 1500°C for 1 hour in an atmosphere of hydrogen saturated with water vapor at 23°C sufficed to produce a good bond over most of the interface. Sintering with the uranium bond was not possible in dry hydrogen or in vacuum.
Due to contraction of the liquid uranium into the void space between the two wafers and the lack of wetting of the oxide by the metal, the periphery of the interface between the two wafers was not completely bonded. This introduced a contact resistance into the transport process which had to be accounted for in the data analysis. The metallic uranium reacted with water from the moist hydrogen and was converted to oxide at the interface. A single specimen was used for all experiments.

Following the activity distribution measurement after each anneal, the enriched and depleted faces of the duplex specimen were ground to a mirror finish with abrasives. Sufficient material (~10 μm) was removed in this process to return the alpha radioactivity of each face to the value characteristic of the original materials. The duplex specimen was cleaned ultrasonically in methanol and loaded into the rig shown in Fig. 1, which was then heated in a tungsten resistance furnace. Holes in bottom of the crucible permitted access of the slowly-flowing gas to the specimen. A key feature of the apparatus was the rhenium foils (25 μm thick) which covered both faces of the specimen. These were designed to eliminate UO₂ vaporization and vapor transport of the tracer during the anneals. There was essentially no gap between the foils and the specimen faces; the foils adhered to the UO₂ faces but could be peeled off following an experiment.

In conducting an anneal, the system was first heated to ~1000°C for about 10 minutes for degassing and then the temperature was quickly raised to the desired value. The anneals ranged in duration from 2 hours
at 1760°C to 15 minutes at 2100°C. In the set of experiments covering this temperature range, the gas contacting the specimen was hydrogen saturated with water at 23°C. In a second set of experiments, the temperature was fixed at 1815°C and anneals were conducted in atmospheres of xenon, krypton, argon and helium at 1 atm. Finally, one experiment in vacuum was performed.

Following each anneal, the radial distribution of alpha activity on the depleted face of the duplex specimen was measured using the aperture technique of Marlowe and Kaznoff (6). The enriched face and the specimen sides were covered with scotch tape, which sufficed to block all alpha particles from these surfaces from contributing to the count rate. The depleted face was partially covered with one of a series of brass disks 75 µm thick with apertures diameters ranging from 3 mm to 14 mm. The alpha radioactivity of the uncovered portion of the sample surface was measured in a gas flow proportional counter. The activities of the enriched and depleted faces (following polishing to remove the activity distributions caused by previous anneal) were measured in the same counter.

**DATA REDUCTION**

For use of the theory, the aperture count rate data had to be deconvoluted to provide a measure of the local flux of alpha particles leaving a unit area of surface as a function of radial position on the initially depleted surface. The quantity provided by the theory is the dimensionless countrate:

\[
R = \frac{I - I_d}{I_e - I_d} \tag{1}
\]
where \( I \) is the current of alpha particles leaving the surface at radius \( r \) and the quantities \( I_e \) and \( I_d \) are the comparable currents from the surfaces of the original enriched and depleted materials, respectively.

The countrates measured with an aperture of radius \( r \) are integrals of the currents:

\[
J(r) = 2\pi \int_0^r I(r') r'dr' \tag{2}
\]

To deduce \( I(r) \) from the 8 or 9 measurements of \( J(r) \), the former was assumed to be represented by the polynomial:

\[
I(r) = A_0 + A_2 r^2 + A_3 r^3 \tag{3}
\]

Because the activity distribution must exhibit a minimum at the origin, no linear term is included in Eq(3) and in addition, the parameter \( A_2 \) must be positive. Inserting Eq(3) into Eq(2) yields the equation to which the radioactivity measurements were fitted:

\[
J(r) = 2\pi \left( \frac{1}{2} A_0 r^2 + \frac{1}{4} A_2 r^4 + \frac{1}{5} A_3 r^5 \right) \tag{4}
\]

If the fitting procedure produced a negative value of \( A_2 \), this parameter was set equal to zero and the data fitted to the two-parameter polynomial involving only the constants \( A_0 \) and \( A_3 \). Once the coefficients had been determined from the data, the dimensionless countrate given by Eq (1) was computed as a function of radial position. Values of \( I_e \) and \( I_d \) were measured prior to each anneal, but only small variations from similar measurements for previous experiments were noted.

The results of all experiments are shown in Table 1. The runs
are numbered in the order that the tests were conducted. This may be significant because the same duplex specimen was used for all experiments. The fourth row indicates that the gaseous environment was wet hydrogen for the 8 experiments in which temperature was varied. The remaining runs were at the same temperature but used different ambient gases. The initial sample radius was 7.3 mm. Following run no. 6, the sample was remeasured and found to have been reduced by 0.8 mm in diameter due to the grinding operation used to prepare the specimen for each new run. The radii of the apertures used to mask portions of the depleted wafter surface during alpha counting are listed in the first column of Table 1. The counts recorded in 8 minutes from each aperture (which are the values of J in Eq (4)) are listed in the remainder of the table.

**TRACER SPREADING MODEL**

In addition to azimuthal symmetry, the geometry of the duplex specimen is symmetric about the midplane. Thus, only the depleted half, which consisted of a cylindrical side of height \( \lambda \) and radius \( a \) and a circular surface of the same radius, needs to be treated. Because the wafers are thin (\( a/\lambda = 7 \)), the two-region geometry can be approximated by a single circular region of the same area as the actual surface. The equivalent radius is:

\[
\frac{a^2}{\text{eff}} = a^2 + 2a\lambda
\]  

(5)

The tracer atom balance on this surface is:

\[
\frac{\partial c^+}{\partial t} = D_s \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c^+}{\partial r} \right) + D_v \left( \frac{\partial c^+}{\partial z} \right)_{z=0}
\]  

(6)
where $C^+_s$ is the tracer surface concentration (atoms per unit area) at radial location $r$ and $C_v$ is the bulk tracer concentration (atoms per unit volume) at radial position $r$ and penetration depth $z$. $D_s$ and $D_v$ are the surface and bulk diffusion coefficients of uranium on or in UO$_2$. Since the specimen was polycrystalline, the latter reflects contributions from lattice and grain boundary diffusion. Because of the masking technique described earlier, both surface evaporation and tracer vapor transport are neglected in Eq(6).

The location $r = a_{\text{eff}}$ is the periphery of the interface between the enriched and depleted wafers. Because this joint is imperfect, the boundary condition here assumes transport across the interface to be determined by an interface conductance $h$ according to the equation:

$$D_s \left( \frac{dC^+_s}{dr} \right)_{r=a_{\text{eff}}} = h \left[ (C^+_s)^m - (C^+_s)_{r=a_{\text{eff}}} \right] \quad (7)$$

where $(C^+_s)^m$ is the hypothetical surface concentration in the midplane of the specimen periphery and $(C^+_s)_{r=a_{\text{eff}}}$ is the actual tracer surface concentration on the depleted wafer side of this interface.

The dimensionless surface tracer concentration is defined by:

$$u = \frac{C^+_s/C_s - q_d}{q_e - q_d} \quad (8)$$

where $C_s$ is the number of atoms of uranium per unit area of the UO$_2$ surface and $q_e$ and $q_d$ are the U-235 fractions of the enriched and depleted wafers, respectively.
The comparable dimensionless bulk tracer concentration is:

\[ v = \frac{C_v^+/C_v - q_d}{q_e - q_d} \]  \hspace{1cm} (9)

where \( C_v \) is the number of uranium atoms per unit volume in \( \text{UO}_2 \).

Radial position is nondimensionalized by the effective radius of the specimen:

\[ n = r/a_{\text{eff}} \]  \hspace{1cm} (10)

Penetration depth is expressed in terms of the alpha particle range in \( \text{UO}_2 \), \( z_F \):

\[ Z = z/z_F \]  \hspace{1cm} (11)

and the dimensionless time is:

\[ \tau = D_v t/z_F^2 \]  \hspace{1cm} (12)

The dimensionless form of Eq(6) is:

\[ \text{EG} \frac{\partial^2 u}{\partial \tau^2} = \frac{1}{\gamma} \frac{\partial}{\partial \gamma} \left( \gamma \frac{\partial u}{\partial \gamma} \right) + \frac{\partial}{\partial Z} E \left( \frac{\partial v}{\partial Z} \right) \bigg|_{Z=0} \]  \hspace{1cm} (13)
where

\[ E = \frac{a_{\text{eff}}^2 D_v C_v}{\sqrt{\pi} z_F D_s C_s} \quad (14) \]

\[ G = \frac{C_s}{z_F C_v} \quad (15) \]

The parameter \( G \) consists of known physical properties and is equal to \( 5 \times 10^{-5} \).

Fick's second law for tracer diffusion in the bulk is:

\[ \frac{\partial v}{\partial t} = \frac{\partial^2 v}{\partial Z^2} \quad (16) \]

for which the initial condition (for the depleted face to the specimen) is

\[ v(Z,0) = 0 \quad (17) \]

and the boundary conditions are:

\[ v(0,\tau) = u(\eta,\tau) \quad (18) \]

and

\[ v(\infty,\tau) = 0 \quad (19) \]
Eq (18) requires that the isotopic content of the solid be continuous as the bulk meets the surface and Eq (19) reflects the fact that the depth of penetration of tracer into the depleted face is very small compared to the specimen thickness.

The solution of Eqs (16) - (19) is:

\[ v = \frac{2}{\sqrt{\pi}} \int_{Z/2\sqrt{\pi}}^{\infty} u(\eta, z - z^2/4x^2) \, e^{-x^2} \, dx \]  

This is Eq (14) of Ref. 10 with no evaporation and a term \( \exp(-x^2) \), which had been inadvertently omitted, added. An accurate approximation of the \( u \)-function in the integrand is obtained from a two-term Taylor series expansion (10):

\[ u(\eta, z - z^2/4x^2) \equiv u(\eta, z) - \frac{Z^2}{4x^2} \frac{\partial u}{\partial x} \]  

Substituting Eq (21) into Eq (20) and differentiating with respect to \( Z \) yields:

\[ \left( \frac{\partial v}{\partial Z} \right)_{Z=0} = -\left( \frac{u}{\sqrt{\pi} z} + \sqrt{\frac{z}{\pi}} \frac{\partial u}{\partial \eta} \right) \]  

Use of this form in Eq (13) gives:

\[ E(\sqrt{z} + G) \frac{\partial u}{\partial \tau} = \frac{1}{\eta} \frac{\partial}{\partial \eta} \left( \eta \frac{\partial u}{\partial \eta} \right) - \frac{E}{\eta} \frac{\partial u}{\partial \tau} \]  

(23)
The initial and boundary conditions are:

\[ u(\eta, 0) = 0 \]  
\[ \left( \frac{\partial u}{\partial \eta} \right)_{\eta=0} = 0 \]  

Because of symmetry about the midplane of the duplex specimen, the right hand side of Eq(8) is one half when \( C^+_s \) is replaced by the midplane value \( (C^+_s)_m \), or from Eq(7):

\[ \left( \frac{\partial u}{\partial \eta} \right)_{\eta=1} = H \left[ \frac{1}{2} - u(1, z) \right] \]  

where

\[ H = \frac{h a_{\text{eff}}}{D_s} \]

is the dimensionless conductance of the periphery of the joint between the two wafers.

As shown in Ref. 10, the solution \( u(\eta, \tau) \) obtained (numerically) from Eqs(23) - (26) determines the dimensionless countrate of Eq(1) according to the double integral:

\[ R = \frac{4}{\pi^4} \int_0^1 (1-Z) dZ \int_0^\infty u(\eta, z - Z^2/4x^2) e^{-x^2} dx \]  

Using Eq(21) permits this integral to be performed and the theoretical
value of \( R \) is given by:

\[
R = Q u + S \frac{\partial u}{\partial \tau}
\]  

(29)

where, for the small values of \( \tau \) encountered in the present application:

\[
Q = 4 \sqrt{2} \left( \frac{1}{\sqrt{\pi}} - \frac{\sqrt{\pi}}{2} \right)
\]  

(30)

\[
S = - \frac{4}{3\sqrt{\pi}} \tau^{3/2} + \tau^2
\]  

(31)

The approximate form represented by Eqs(29) - (31) has been compared to numerical integration of Eq(28) and found to be accurate to within a few percent.

**DATA ANALYSIS AND RESULTS**

The data collected in Table 1 contain information on the three principal physical properties controlling the uranium isotope exchange process, namely the surface diffusion coefficient \( D_s \), the bulk diffusion coefficient \( D_v \) and the interfacial conductance \( h \). The surface diffusivity is responsible for the high mobility of the uranium, by which transport over distances characteristic of the specimen diameter in times measured in hours is made possible. Bulk diffusion enters the overall process in two ways. Firstly, it provides a sink term in the uranium surface balance (Eq(6)). Secondly, it controls accumulation of tracer beneath the surface, to which the detection system responds. The surface diffusion process is measurable
only if bulk diffusion of uranium is neither too large nor too small. If bulk diffusion of uranium is rapid, the tracer that enters the surface of the depleted wafer from the enriched one is quickly removed by diffusion into the bulk solid near the wafer-wafer interface and little reaches far onto the face of the depleted wafer. If the bulk diffusion coefficient is small, surface spreading of the tracer across the face of the depleted wafer occurs easily but is not measurable because none is absorbed beneath the surface.

Instead of the physical parameters $D_s$, $D_v$ and $h$, fitting of the data in Table 1 to the tracer spreading model was performed using the corresponding dimensionless quantities $E$, $\tau$, and $H$. The procedure would have been fairly straightforward were the bulk diffusion coefficient of uranium in $UO_2$ accurately known, for then the dimensionless time would been a known quantity. Despite many measurements of $D_v$ over the past two decades, Matzke's review (11) demonstrates that a broad band of uncertainty in this property remains. However, it is not totally unknown. Therefore, $D_v$ (or $\tau$) has been permitted to be a semi-free parameter in the data fitting procedure, by which is meant constraining the bulk diffusivity within upper and lower limits estimated from Matzke's compilation (11):

$$0.024 \exp(-93/RT) \leq D_v \leq 0.027 \exp(-87/RT)$$

(32)

where $D_v$ is in cm$^2$/s and the activation energies are in kcal/mole. For each run in Table 1, the above restriction produced a band in which the corresponding dimensionless quantity $\tau$ was constrained in the fitting process. The value of the alpha particle range in $UO_2$ was taken to be 10 $\mu$m (10).

For each run, the data in Table 1 were fitted according to Eq(4)
and then recast as dimensionless countrates using Eqs(1) and (3). These data were compared to the predictions of the tracer spreading model embodied in Eq(29). The values of $E$, $\tau$ (within the allowable limits) and $H$ needed in the theoretical model were chosen to best fit the data for each run.

The process of extracting values of $D_s$ from the data was aided by the following observations. First, the parameter $H$ is closely related to the slope of the countrate distribution at the wafer edge (See Eq(26) and (29) with the last terms in each neglected). Consequently, good first trials of this parameter could be estimated directly from the data. Second, the data could be satisfactorily fitted to a range of $E$ and $\tau$ values with a roughly constant ratio of the two. Thus, despite the lack of a unique set $(E, \tau, H)$ which fit the data for each run, a single combination of $\tau/E$ and $H$ was obtainable from the data fitting procedure with an accuracy of about 20% on each. As will be seen later, the reproducibility of the experiments was poorer than this, so that the accuracy of the surface diffusion coefficients reported is not limited by the ability to fit the data to the theory. The surface diffusion coefficient was determined from the best-fit value of the ratio of $\tau$ to $E$ by use of Eqs(12) and (14):

$$D_s = \frac{(\tau/E)z_F^{2}a_{eff}}{\sqrt{\tau}(C_s/C_v)}$$

(33)

where the effective wafer radius is defined by Eq(5) and the ratio of superficial and volumetric uranium concentrations for $\text{UO}_2$ (i.e., $C_s/C_v$)
is $2.7 \times 10^{-8}$ cm.

Figure 2 shows the steps in the fitting process for the temperature variation runs in Table 1. In each graph, the countrate data and the polynomial fit by Eq(4) are shown on the left. In some cases both two-and three-parameters fits could be obtained. However, these fits were indistinguishable from each other on the scale of the drawing and are shown as single curves. The points on the right hand portions of the drawings correspond to the radial distributions of the dimensionless countrate obtained from Eqs(1) and (3). While these points do not strictly speaking represent discrete data, they have been plotted as such to facilitate comparison with the theoretical results. In the case that the original data were fitted to both two-and three-parameter polynomials, slight differences in the goodness of the fits which were not visible on the left hand plots are magnified and produced distinct sets of points on the right hand plots. The curves on the right hand plots are the results of the model calculations for the two or three combinations of parameters which best fit the data.

Run numbers 5 and 6 are plotted on the same graph in Fig. 2 because they represent replicate experiments. Except for these runs and the highest temperature experiment (run 8), very close model fits to the data were obtained. The raw data for run 8 do not appear different in general shape from those for the experiments at lower temperatures, but the dimensionless countrate distribution derived from these data is concave downward rather than concave upward. The former shape cannot be properly fitted by the theory.

Table 2 summarizes the parameters of the best-fitting theoretical curves shown on the right hand sides of the graphs in Fig. 2. Despite
the range of \( E \) and \( \tau \) values which can fit the same set of data, the \( \tau/E \) ratios for a particular experiment are generally much less variable. The surface diffusion coefficients calculated from Eq(33) are listed in the last column of Table 2 and are plotted in Fig. 3. Also shown on this graph is the datum at 1915°C obtained by Marlowe and Kaznoff (6) after reinterpretation in Ref. 10 by the same type of theoretical model as was applied to the present data. The good agreement between the results of the two tracer experiments demonstrates that the theoretical model used for analysis of the data can accommodate quite different geometries of the diffusion couple. The good accord also shows that neither evaporation of the specimens nor isotope movement by vapor transport affected the present tests or those of Marlowe and Kaznoff. Not only did the close-fitting rhenium foils (Fig. 1) prevent transport in the gas phase, but they did not introduce spurious effects such as impeding surface diffusion by physically contacting the \( \text{UO}_2 \) surfaces or providing a parallel surface diffusion pathway.

The diffusion coefficient can be expressed in Arrhenius form:

\[
D_s = D_{s0} \exp\left(-\frac{E_s}{RT}\right)
\]  

(34)

The line through the data in Fig. 3 corresponds to \( D_{s0} = 5 \times 10^6 \text{ cm}^2/\text{s} \) and \( E_s = 72 \text{ kcal/mole} \). Although the deviations of the data points from the line are generally within \( \pm 50\% \), the errors in the coefficients in Eq(34) are larger. The accuracy of \( E_s \) is estimated to be \( \approx \pm 15 \text{ kcal/mole} \) and \( D_{s0} \) is not known to better than one or two orders of magnitude about the mean value. Nevertheless, both the preexponential factor and the activation energy are significantly smaller than previous measurements of surface diffusion on \( \text{UO}_2 \)(4,5).

The value of \( \tau \) listed in Table 2 which provided the best fitting model curves correspond to bulk diffusion coefficients which are plotted in Fig. 4 as bars for each run along with the bounding lines given by Eq(32). Adequate data interpretation was achieved with values of \( D_v \).
within the range of previous measurements from the literature (11). The bulk diffusivities of the urania in the duplex specimen used in the present work are on the low side of the band representing the results of experiments designed solely to measure this property. However, the bars in Fig. 4 should not be construed as measurements of $D_v$.

Figures 5 - 8 and Table 3 show the data and the derived surface diffusion coefficients for the measurements in a variety of atmospheres at a fixed temperature. As in the previous tests in wet hydrogen at varying temperature, the theory was readily fitted to the data. There does not, however, appear to be a clear effect of the ambient gas (or lack of it) on the surface diffusion coefficient. Except for the result in argon, the $D_s$ values in Table 3 are lower than the range of values of $D_s$ in wet hydrogen at the same temperature. The limited extent of tracer movement in helium and vacuum environments is unexpected. Note that these gases contained no reducing agent nor were they highly dried prior to introduction into the furnace.

Examination of the values of the interfacial resistance parameter ($H$) given in Tables 2 and 3 shows no particular variation with either temperature or gaseous environment. Values between 0.02 and 0.15 appear in both Tables. The extent to which the resistance of the joint impedes surface movement of uranium between the enriched and depleted wafers comprising the diffusion couple can be assessed by calculating the dimensionless count rate expected at the specimen periphery had there been a perfect joint. If $H$ were very large, Eq(26) shows that $u(1,\tau) = \frac{1}{2}$ and Eq(29) reduces to $R(\eta=1) = Q/2$, where, for small $\tau$, $Q = 4(\tau/\pi)^{1/2}$. If the interface had offered no transport resistance, at the experimental $\tau$ values ranging from 0.02 to 0.04 (Table 2), values of $R$ at $\eta = 1$ between 0.2 and 0.4 should have been observed. However, examination of
of the right hand plots in Fig. 2 shows that the actual dimensionless counts rates at a fractional radius of one are less than 5% of these values. The interface is thus a larger impediment to surface spreading of uranium isotopes than is surface diffusion.

DISCUSSION

The very large preexponential factor for surface diffusion on UO₂ is characteristic of many ceramic oxides(7). In the framework of the conventional site-to-site hopping mechanism of atom migration universally applicable to volume diffusion in solids, the large preexponential factor implies an enormous jump distance on the surface. Similar observations have been reported for surface diffusion on some metals, for which Bonzel(17) developed a theory of surface diffusion out which naturally arises very large preexponential factors.

Bonzel's model is based upon the assumption that only surface atoms (or polyatomic units built up from the atoms or ions of the crystal) which are in an adsorbed state (adatoms) are responsible for surface mobility. The vast majority of the ∼ 10^{15} surface atoms per square centimeter form part of the terrace-ledge-kink surface structure. An equilibrium fraction of surface atoms in the adatom state ($f_a$) is maintained by the ledges acting as source and sink:

$$f_a = \exp(\Delta S_a / R) \exp(-\Delta H_a / RT)$$

(35)

where $R$ is the gas constant and $\Delta S_a$ and $\Delta H_a$ are the entropy and enthalpy of formation of the adatoms from the atoms in the surface. Surface-adsorbed single atoms are treated as three-dimensional oscillators with two degrees of vibrational motion parallel to the surface and a third normal to it. An adsorbed molecule such as a UO₂ possesses these three center-of-mass vibrational modes but in addition exhibits internal vi-
The surface diffusion coefficient is given by:

\[ D_s = f_a D^* \]  

(36)

where \( D^* \) is the intrinsic diffusion coefficient of the adatom. This formulation is analogous to the "equilibrium trapping" model frequently applied to fission gas diffusion in \( \text{UO}_2 \)\(^{18} \). Bonzel shows how to calculate \( D^* \) for the case of localized motion (hopping one lattice position at a time) and for the case of nonlocalized migration, in which long distances are traversed between leaving and returning to the adatom state. Only the latter mechanism produces large preexponential factors characteristic of surface migration on \( \text{UO}_2 \).

Bonzel's model starts from the equation for the intrinsic diffusion coefficient of the adatom in nonlocalized motion obtained from random walk theory:

\[ D^* = \alpha l^2 \Gamma \]  

(37)

where \( \alpha \) is a geometrical constant (set equal to unity), and \( l \) and \( \Gamma \) are the jump distance and the jump frequency, respectively. These two properties of the adatom are determined with the aid of absolute rate theory, according to which motion occurs by population of an activated state from the adatom state. The nonlocalized activated state is a two-dimensional zone with an area of approximately one lattice constant squared. A molecule in this state has an energy \( \Delta H^* \) above that of the equilibrium adatom state (Fig. 9). The average two-dimensional thermal velocity of the molecules in the activated
state is:

\[ \nu = 2 \sqrt{\frac{kT}{\pi m}} \]  
(38)

where \( k \) is Boltzmann's constant and \( m = 4.5 \times 10^{-22} \) g is the mass of the \( \text{UO}_2 \) molecule. The intrinsic diffusion coefficient obtained by Bonzel is:

\[ D^* = \frac{\alpha \nu^2}{\nu_1} \left( \frac{z^*_a}{z_a} \right) \exp \left( - \frac{\Delta H^*}{RT} \right) \]  
(39)

where \( \nu \) is the vibration frequency of the equilibrium adatom perpendicular to the surface and \( z_a \) is its partition function:

\[ z_a = \left( \frac{kT}{\hbar \nu_1} \right)^2 \frac{z_{\text{vib}}}{z_{\text{int}}} \]  
(40)

where \( \hbar \) is Planck's constant, \( \nu_{11} \) is the frequency of adatom vibration parallel to the surface and \( z_{\text{vib}} \) is the partition function representing the three internal vibrational modes of the linear \( \text{UO}_2 \) molecule stretching and bending modes, see Ref. 19). The form of the center-of-mass vibrational partition functions in Eq(40) assumes that \( kT \gg \hbar \nu \), which appears to be a satisfactory simplification. The degrees of freedom of the molecule in the nonlocalized activated state include vibration normal to the surface, internal vibrational modes, two translational modes, and rotational modes. The first two of these are present in the adsorbed state, but the two parallel vibrational modes of the equilibrium adsorbed species have been replaced by two translational modes and two rotational modes in the activated state.
The partition function of the activated state is:

\[
\zeta^* = \left( \frac{kT}{v} \right)^{\text{vib}} z_{\text{int}} \left( \frac{2\pi mkT_A}{\hbar^2} \right) \left( \frac{T}{2\Theta_{\text{rot}}} \right)
\]

(41)

where \( A = 1.5 \times 10^{-15} \text{ cm}^2 \) is the area per surface uranium atom in the close-packed planes of the \( \text{UO}_2 \) structure. The quantity \( \Theta_{\text{rot}} \) is the temperature characterizing the two degrees of freedom for unhindered rotation of the \( \text{UO}_2 \) molecule in the activated state on the surface. This quantity can be calculated from a standard statistical-mechanical formula for a linear molecule provided that the moment of inertia is known. The latter depends on the masses of the particles at each end of the molecule (oxygen atoms) and on the uranium-oxygen bond distance (1.79 \( \text{Å} \), Ref. 19). The rotational temperature of the \( \text{UO}_2 \) molecule is calculated to be 0.24 K.

Assuming \( v_\uparrow = v_\downarrow \) and \( z_{\text{vib}}^\text{vib} \) to be the same in the equilibrium adatom and the activated states, the partition function ratio in Eq(39) becomes:

\[
\frac{z^*}{z_a} = \left( \frac{2\pi mkT_A}{\hbar^2} \right) \left( \frac{T}{2\Theta_{\text{rot}}} \right)
\]

(42)

Taking \( T \) to be the average temperature of the tracer spreading experiments (2200 K) and assuming \( v_{11} = 10^{13} \text{ s}^{-1} \), the partition functions in the above equation are 30,000 for translation, 4600 for rotation and \((4.6)^2 \) for vibration. The ratio \( z^*/z_a \) is \( 6.5 \times 10^6 \). Taking \( \alpha = 1 \), calculating \( v = 2.9 \times 10^4 \text{ cm/s} \) from Eq (38) and assuming \( v_\downarrow = 10^{13} \text{s}^{-1} \), the pre-
exponential factor of $D^*$ in Eq(39) is $D^*_0 = 3.6 \times 10^9$ cm$^2$/s.

According to Eqs(35) and (36), the preexponential factor of $D_s$ is equal to $D^*_0 \exp (\Delta S_a / R)$. In the case of a metal lattice supporting a population of single adsorbed atoms, Bonzel takes $\Delta S_a = 1.5R$, in which is implicit the reasonable expectation that little change in the vibrational entropy occurs when an atom is moved from a kink site to an adsorbed site. For uranium dioxide, on the other hand, the moving unit is assumed to be the neutral UO$_2$ molecule, and the entropy change associated with assembling this surface-adsorbed species from the constituent ions in the surface structure may be very much different from that for producing an adatom on a metal surface.

The entropy change $\Delta S_a$ can be computed from the thermodynamic cycle shown in Fig. 9, which gives:

$$\Delta S_a = \Delta S_v - (S_g - S_a)$$  \hspace{1cm} (43)

where $\Delta S_v = 39.3$ eu is the entropy of vaporization of UO$_2$ and $S_g$ is the absolute entropy of the UO$_2$ molecule in its gaseous standard state, which consists of contributions due to translation, rotation and internal, rotation and internal vibrations:

$$S_g = S_{tr} + S_{rot} + S_{\text{int}}^{\text{vib}}$$  \hspace{1cm} (44)

The entropy of the adsorbed UO$_2$ molecule is:

$$S = S_{\text{COM}}^{\text{vib}} + S_{\text{int}}^{\text{vib}}$$  \hspace{1cm} (45)

The last terms in Eqs(44) and (45) represent the entropy due to inter-
nal vibrations of the UO$_2$ molecule, which is assumed to be the same in the adsorbed and gaseous states. The entropy of formation of the surface-adsorbed UO$_2$ molecules is thus:

$$\Delta S_a = \Delta S_V - S_{tr} - S_{rot} + S_{vib}^{\text{COM}}$$

(46)

The translational entropy of the ideal gas can be calculated from statistical mechanical formulas. At the standard conditions of 1 atm pressure and 2200 K, $S_{tr} = 52.7$ eu. The rotational and vibrational entropy contributions are calculated from the formula:

$$S = R \left( \ln z + \frac{\text{dlnz}}{\text{dlnT}} \right)$$

(47)

where $z$ is the appropriate partition function. Using the last term in Eq(41) for $z_{\text{rot}}$, Eq(47) yields $S_{\text{rot}} = 18.7$ eu at 2200 K. Applying the same formula to the center-of-mass vibrational partition functions in Eq(40) (taking $v_\perp = v_{\text{ll}} = 10^{13}$ s$^{-1}$ and $T = 2200$ K) yields $S_{\text{vib}}^{\text{COM}} = 15.0$ eu.

Substituting the numerical values of the component entropies determined above into Eq(46) gives $\Delta S_a = -17.1$ eu. The large negative entropy of formation of the UO$_2$ is a reflection of the more organized state of the neutral UO$_2$ molecule compared to $\text{U}^{4+}$ and $\text{O}^{2-}$ ions in the crystal lattice at the surface. For comparison, the same method can be used to compute the entropy of formation of copper adatoms on Cu(110).

In this case, the component entropies (at 1200K) are:

$\Delta S_V = 30.3$ eu; $S_{tr} = 45.5$ eu; $S_{rot} = 0$; $S_{\text{vib}}^{\text{COM}} = 17.7$ eu (using the adatom vibration frequencies recommended by Bonzel(17)). Inserting these values into Eq(46) yields $\Delta S_a = 2.5$ eu, which is in good agreement with the value of 3.0 eu used by Bonzel.
The theoretical preexponential factor in Eq(34) is:

\[ D_{so} = D_0 \exp(\Delta S_a/R) = 3.6 \times 10^9 e^{-17.1/R} = 6.6 \times 10^5 \text{ cm}^2/\text{s} \]

If the calculation is repeated with a COM vibration frequency of \(5 \times 10^{12} \text{ s}^{-1}\), the resulting calculated value of \(D_{so}\) is \(7.6 \times 10^5 \text{ cm}^2/\text{s}\).

Comparing these theoretical values with the observed Arrhenius form of \(D_s\) given by Eq(34), the preexponential factor is seen to be underpredicted by a factor of \(\sim 7\). This discrepancy corresponds to an error of \(\sim 4\) eu in \(\Delta S_a\) or in the corresponding entropy terms in \(D_0\). Noting that these entropies result from adding and subtracting a number of fairly large component entropies, an error of 4 eu is not unreasonable. In addition the accuracy of the experiment preexponential factor is larger than the discrepancy with theory. In sum, it can be concluded that Bonzel's model of nonlocalized surface diffusion applies quantitatively to UO\(_2\) if the migrating species used in the computations is the neutral UO\(_2\) molecule.

According to the diffusion model, the observed activation energy of surface diffusion is the sum of the enthalpy of formation of the adatom and the activation enthalpy of the nonlocalized state:

\[ E_s = \Delta H_a + \Delta H^* \quad (49) \]

Not enough is known about the interatomic forces on the UO\(_2\) surface to permit calculation of either of the two terms on the right hand side OF Eq(49). The experimental results show only that their sum is \(\sim 72\) kcal/mole.

The model calculations described above were based upon the assumption that the adatom is the UO\(_2\) molecule. A similar calculation can be performed with the U\(^{+4}\) ion as the migrating species. In this case, the entropy of formation of the equilibrium adatom is approximated by
the 3 eu which characterizes the copper adatom. However, the partition function for the activated state contains no rotational component, so the second term in the numerator of Eq(42) is removed in computing $z^*/z_a$. The resulting theoretical value of $D_{so}$ is $<10^3$ cm$^2$/s, far smaller than the experimental result. It appears that the rotational stabilization achievable only by a polyatomic entity such as the UO$_2$ molecule is necessary for the high surface mobility on this oxide.

A consequence of Bonzel's model which bears examination is the "jump distance" in Eq(37). For surface diffusion by the nonlocalized mode, this quantity is more precisely termed the mean free path in the two-dimensional gas between activation and deactivation. The theory is not specific on the cause of deactivation of the moving species. Bonzel suggests collision with another moving molecule, a two-dimensional analog of the principal event in a common three-dimensional ideal gas. Or, the moving molecule may encounter a localized adatom. However, Bonzel's model does not allow for the effect of morphological features of the surface on the mean free path of the migrating species. Such features include ledges, emerging dislocations, impurity atoms on the surface, and grain boundaries. Were any of these defects to serve as collision partners for the moving species, the mean free path of the latter would depend on a measure of the density of the obstacles, as neutron diffusion in a moderator is dependent on the density of moderator atoms. Bonzel's theory does not permit this type of deactivation, but instead determines the mean free path solely from the properties of the surface molecule in the adatom and activated states. The mean free path can be obtained by equating the right hand sides of Eqs(37) and (39) and using $\Gamma = v_\perp \exp(-\Delta H^*/RT)$, leading to:

$$l = \frac{v_\perp z^*}{v_\perp z_a}$$

(49)
All of the quantities on the right hand side of this equation have been calculated previously. Their use gives mean free path between 100 and 200 μm, depending on the value of v employed. Application of Bonzel's to UO₂ implies that an activated UO₂ molecule can travel as an ideal gas particle for distances which traverse 10 to 20 grain boundaries, not to mention a much larger number of small structural defects which undoubtedly are present on the grain faces. The theory thus suggest a remarkably deactivation-resistant surface species on UO₂. Since Bonzel's theory is structure-insensitive, surface diffusion on single crystals of uranium dioxide should be the same as on polycrystals. The feature of the theory remains to be tested.

Another extrinsic mechanism of deactivation of moving surface species is collision with gas atoms impinging on the surface. The series of experiments in which the ambient gas was varied was intended to examine this possibility. It is reasonable to assume that the surface diffusivity decreases with increasing frequency of collision of gas atoms with the surface in a manner similar to the inverse dependence of gas phase diffusion on total pressure. Accordingly, Dₛ should be largest in a vacuum, change in a regular fashion as the atomic weight of the gas is varied at constant pressure, and decrease with increasing pressure of a single gas. The present experiments bore out none of these expectations, so it is useful to query the theory to ascertain whether a change of sufficient magnitude to stand out from experimental uncertainties should have been expected in the conditions of the gas-variation tests.

In a vacuum, the moving species has a natural mean free path on the surface (Eq(49)) which is independent of the environment. To determine how this flight path is shortened by the presence of a gas above the solid, the probability of premature deactivation by collision with impinging gas atoms is calculated. This probability is the prod-
duct of two others. The first is the probability that a moving surface molecule is struck by an impinging gas atom and the second is the probability that the collision removes sufficient energy from the former to cause it to return to the bound adatom state.

During its flight across the surface, a moving adatom presents a rectangular area of length equal to its natural mean free path \( \lambda \) and width equal to the collision diameter with the gas atom, \( \sigma \). Assuming hard sphere collisions, the collision diameter is the sum of the molecular diameter of the \( \text{UO}_2 \) molecule \( (d_U) \) and the atomic diameter of the gas atom \( (d_g) \):

\[
\sigma = d_U + d_g
\]  

(50)

If a gas atom strikes the area \( \sigma \lambda \) while the surface molecule is moving across its track, a collision is possible.

The impingement rate of the gas on the surface for 1 atm pressure and 2200 K is:

\[
Q = \frac{p}{\sqrt{2\pi m g k T}} = \frac{5.7 \times 10^{23}}{\sqrt{M_g}} \text{ atoms/cm}^2 \cdot \text{s}
\]  

(51)

where \( M_g \) is the atomic weight of the gas. The lifetime of the moving molecule on the surface is \( \lambda/v \), where \( v \) is its thermal velocity, so that the total number of gas atom which strike the path of the moving molecule during its flight along its natural path length is \( Q(\sigma \lambda) \) \( (\lambda/v) \).

the probability that any one of these impinging atoms collides with the moving surface molecule is the ratio of the collision diameter to the path length, or to \( \sigma/\lambda \). Multiplying these two probabilities, the probability that a moving surface molecule is struck by an impinging
gas atom before it naturally deactivates is:

\[ P_{\text{coll}} = \frac{Q \sigma^2}{v} \]  \hspace{1cm} (52)

Taking \( M_g = 132 \) (for xenon), \( \sigma = 4 \, \text{Å} \), \( \lambda = 150 \, \text{µm} \), and \( v = 2.9 \times 10^4 \, \text{cm/s} \), Eq(52) gives a \( P_{\text{coll}} \sim 40 \), implying a very high likelihood of a collision. Because of the atomic weight factor in Eq(51), the collision probability is even higher for gases lighter than xenon.

However, not every collision need result in deactivation. Energy transfer in the collision is more efficient for the heavy species (which have masses closer to that of the \( \text{UO}_2 \) molecule) than the lighter ones, as determined by the energy transfer factor \( 4M_g M_U / (M_g + M_U)^2 \), where \( M_U \) is the molecular weight of \( \text{UO}_2 \). Lacking knowledge of the energy transfer mechanism in such collisions and the translational energy that must be removed from the moving surface molecule to cause deactivation, quantitative assessment of the probability of deactivation in a collision is not possible. However, it is quite likely that the lighter gases are less efficient in this respect than the heavier ones. In addition, the probability of removing an appreciable fraction of the activation enthalpy \( \Delta H^* \) of the moving \( \text{UO}_2 \) molecule by collision with a gas atom is undoubtedly considerably less than unity, so the product of this factor and \( P_{\text{coll}} \) of Eq(52) may also be less than one. If so, the theory would be consistent with the failure to observe a significant effect of the gaseous environment on surface diffusion. However, if the gas pressure were very high, as it is in fission gas bubbles, it is possible that the correspondingly larger collision probabilities could cause a decrease in surface mobility, as postulated in Refs. 12-14.
CONCLUSIONS

The surface diffusion coefficient on polycrystalline UO$_2$ has been determined by measurement of the spreading of tracer uranium on the surface of a duplex specimen composed of enriched and depleted UO$_2$ wafers. Surface diffusivities were determined from the data by means of a phenomenological model which included simultaneous bulk diffusion and an interface resistance between the two wafers. The surface diffusion coefficients over the temperature interval from 1760 to 2100°C range from $\sim 0.1$ to $\sim 2$ cm$^2$/s. The quantity needed in analyses of mass transport along the surface is the product of $D_s$ and the surface layer thickness $\delta$, which in the present model is equal to the ratio of the areal density of uranium atoms on the surface to the bulk uranium atom density in the solid. This ratio is $\sim 3\, \text{Å}$. Consequently, the product $\delta D_s$ varies from $3 \times 10^{-9}$ to $6 \times 10^{-8}$ cm$^3$/s over the temperature range investigated.

Bonzel's theory of nonlocalized surface migration was applied to the measurements and was found to be capable of explaining the large preexponential factor of $D_s$ provided that the migrating species is the UO$_2$ molecule capable of free rotation. However, a consequence of this requirement is a long mean free path of the migrating molecule on the surface, which covers distances equivalent to many grains between activation to the nonlocalized mobile state and deactivation back to the bound adatom state. This very large predicted mean free path is directly related to the assumption of unhindered rotation of the activated UO$_2$ molecule on the surface. If one degree of rotational freedom is removed from the partition function $z^*$, a physically acceptable (but still quite large) mean free path results. However,
removal of one degree of rotational freedom results in a substantial decrease in the calculated preexponential factor, and agreement of experiment with theory is lost. In order to reduce the mean free path by invoking hindered rotation yet maintain the necessary large preexponential factor, a smaller entropy of formation of the bound adatom state ($\Delta S_a$) than the value of -17 eu estimated from available information on UO$_2$ vaporization would be needed.

The effect of the nature of the ambient gas on $D_s$, if such an effect was present, was less than the precision of the measurements. The absence of this affect could be rationalized by the theory, however.

ACKNOWLEDGEMENT

This work was supported by the Direct, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract #DE-AC03-76SF0098.
REFERENCES

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19. D.W. Green, "Calculation of the Thermodynamic Properties of Fuel-Vapor
### TABLE 1

#### DATA SUMMARY

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<th>RUN NO.</th>
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#### Preanneal 8 minute counts per cm² (all runs):
- Enriched face: $2,360,000 \pm 5400$
- Depleted face: $12,900 \pm 80$

#### Sample Geometry:
- Radius: 0.73 cm (Run Nos. 1-6); 0.69 cm (Run Nos. 7 - 13)
- Thickness of each disk: 0.1 cm
TABLE 2

RESULTS
FOR THE TEMPERATURE DEPENDENCE OF THE SURFACE DIFFUSIVITY

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* The numbers correspond to the numbered curves in Fig. 2.
TABLE 3
EFFECT OF GASEOUS ENVIRONMENT

AT $T = 1814^\circ C$
t = 1 h

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* The numbers corresponds to numbered curves in Figs. 5 - 8
1. Duplex-wafer diffusion couple with rig for annealing in a furnace. The crucible, sleeve and weight are fabricated of molybdenum.

2. Fitting of tracer spreading data for the experiments in flowing wet hydrogen at various temperatures. The curves through the points (o) in the left hand panels represent 2-or 3-parameter polynomial fits. The points in the right hand panels were obtained from the polynomial fits on the left: ▲ 2-parameter; ● 3-parameter. The curves on the right are theoretical; the numbers identifying each give the parameters used in the computation by referring to Table 2.

3. Tracer surface diffusion coefficients on UO₂ in wet hydrogen atmospheres.

4. Volume diffusion coefficients used in determining surface diffusivity. The band corresponds to Eq(32).

5. Fitting of tracer spreading data at 1813°C in xenon gas at 1 atm. Two-parameter fit to data.

6. Fitting of tracer spreading data at 1817°C in krypton gas at 1 atm. Two-parameter fit to the data.

7. Fitting of tracer spreading data at 1811°C in argon gas at 1 atm. Two-parameter (●) and three-parameter (▲) fits to the data.

8. Fitting of tracer spreading data at 1816°C in helium at atm (top) and at 1814°C in vacuum (bottom). Two-parameter fits to the data.

9. Thermodynamic cycle for determining the adatom entropy of formation.
Figure 2.
Figure 2 (continued)
Figure 3.

- This work
- Marlowe and Kaznoff
Figure 4.
Run No. 9 (Xe)

Counts in 8 min $\times 10^{-4}$

Aperture Radius (cm)

Dimensionless Count rate $\times 10^3$

Fractional Radius

Figure 5.
Figure 6.

Run No. 10 (Kr)

Counts in 8 min \times 10^{-4}

Aperture Radius (cm)

Dimensionless Count rate \times 10^3

Fractional Radius

Figure 6.
Run No. II (Ar)

Figure 7.
Figure 8.
Figure 9.
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