Chapter 3

Diffusion in uranium oxides

Our aim is to predict diffusion coefficients of solute ions in ceramic materials. In order to achieve this, we need to consider many aspects of diffusion: the solution site of the ion, the possibility of large defect clusters, the diffusion of ions inside these clusters and the migration of vacancies associated with the mechanism. Interstitial diffusion is usually the fastest diffusion mechanism, but many of the fission products we want to investigate are too large or assume too large a charge state to be trapped as interstitials.

To effectively compare simulated activation enthalpies it will be necessary to understand the techniques and circumstances used in literature experiments.

3.1 Diffusion Coefficients

Diffusion is usually described as Fick's second law:

$$\dot{c}(\vec{x}, t) = D \, \nabla^2 c(\vec{x}, t), \tag{3.1}$$

where $\dot{c}$ is the derivative of the concentration with respect to time, c is the position and time dependent concentration, and D is the diffusion coefficient.

D is usually assumed to depend on temperature exponentially, it can be written as the Arrhenius equation:

$$D = D_0 \exp(\frac{-\Delta H_M}{kT}).$$ (3.2)

ΔH_M is the migration activation enthalpy, k is Bolzmann's constant, T is the absolute temperature and D_0 is a pre-exponential term which is related to the attempt frequency for migration. For simple interstitial migration D_0 is proportional to νd^2: the Debye frequency times the jump distance squared.

The value of D_0 is important in determining whether a fitted diffusion coefficient taken from experiment is in fact due to atomic diffusion. In addition a reasonable estimate of D_0 can be used to make an Arrhenius plot using a migration enthalpy predicted by simulation. Thus a quantitative comparison of theory and experiment that goes further than comparing the activation enthalpies can be made.

Migration in UO_2 is in steps of 2.5-4.0 Å and the attempt frequency usually lies between 10^{11} and 10^{14} [s^{-1}]. D_0 is therefore expected to be in the range of 10^{-9} to 10^{-5} [m^2/s] for most migration mechanisms in UO_2.

Most migration mechanisms will be more complex than simple interstitial migration. However, expression 3.2 remains useful because in practice, it can still be fitted successfully to most diffusion data, even if the mechanism considered is complex. The difference is that ΔH_M is then no longer the migration activation energy, but a quantity called the Arrhenius energy:

$$D = D_0 \exp(\frac{-\Delta H_A}{kT}).$$ (3.3)

We can relate the Arrhenius energy to individual parts of a diffusion process. When

considering vacancy assisted migration, we have to take into account the formation of a vacancy assisting cluster as well as the migration of the ion inside this cluster.

Ions employing a vacancy assisted mechanism will typically be trapped in substitutional positions. From this situation, the formation of a diffusion assisting cluster will simply consist of the addition of one or more vacancies to the trapped ion.

Diffusion in such a system now consists of three steps:

- formation of a diffusion assisting cluster,

- internal diffusion of the migrating ion within the cluster and finally

- dissociation of the cluster.

This means that in reality, equation 3.1 describes the behaviour of only a small number of the ions in solution: those associated with a diffusion cluster. The number of ions in solution actually forming a diffusion cluster is dictated by the energy needed to form such a cluster, E_{Form}. This means that the effective concentration of ions actually participating in diffusion as described by 3.1 is:

$$c_{\text{eff}} = ce^{\frac{-E_{\text{Form}}}{kT}},$$

and the effective diffusion coefficient is:

$$D_{eff} = D'_0 e^{-\frac{E_{Form} + \Delta H_M}{kT}}. \tag{3.4}$$

The mechanism is show graphically in Figure 3.1.

For vacancy assisted diffusion, the Arrhenius energy, often quoted in experimental studies, is equal to $E_{\text{Form.}} + \Delta H_M$. The formation energy, $E_{\text{Form.}}$, should be interpreted as the dissociation energy, when dissociation of the cluster is energetically less favourable than association. Since many diffusion processes are possible
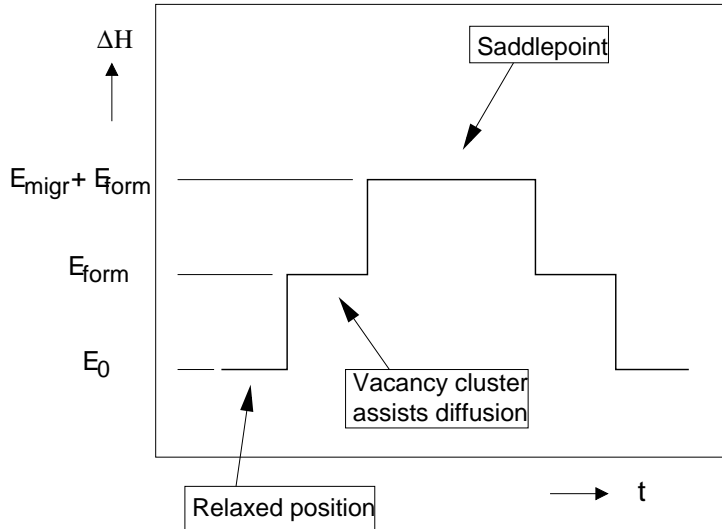
Figure 3.1: An enthalpy-time plot of an assisted diffusion mechanism. A diffusing ion is associated with one or more intrinsic defects, raising the energy of the system. After the formation it migrates over a (now lowered) diffusion path saddle point, followed by dissociation of the cluster into the original defects.

in a material, the final effective diffusion will be a sum of all these processes:

$$\dot{c}(\vec{x}, t) = \sum_i D_{\text{eff},i}(T)\, \nabla^2 c(\vec{x}, t).$$

However, in most cases one process dominates over all others. For example, the activation energy of a vacancy through the host lattice can often be much greater than the energy necessary to move the solute ion through the defect cluster.

3.2   The Association/Dissociation Reaction

The association and dissociation processes are usually symmetric; the dissociation reaction is just the opposite of the association reaction. It is important to make sure that the defects necessary for the reaction to take place are actually available

in the material. Often a Schottky or Frenkel reaction will assist the formation of the cluster. Realistically, E_{Form} will be the difference between the solution enthalpies for the diffusing ion and its diffusion assisting cluster.

Configurational considerations of the cluster association dictate that the pre-exponential parameter, D_0, should change when adapting equation 3.2 for the effective diffusion coefficient (3.4). Finally, E_{Form} will deviate from the equilibrium solution value derived for a stoichiometric material when dealing with non-stoichiometric materials or higher concentrations of impurities [47].

3.3 The Quasi-Harmonic Approach

The Quasi-Harmonic approach (Q-H) of predicting migration activation energies, ΔH_M, is used in this study. By positioning an ion at consecutive positions on the expected diffusion path, and relaxing the lattice around it, a migration activation energy profile is obtained. In some systems, the migration path is obvious due to symmetry, in others an effort has to be made to find it by sampling many positions, and plotting a lowest energy line through the (3-dimensional) saddle point.

3.3.1 Validity of the Q-H Approach

In a real crystal, diffusion is a statistical process. The vibration of the impurity ion and opportunities offered by lattice vibrations control the process. A truly dynamic lattice can be simulated using molecular dynamics (MD) techniques. Starting such a simulation with a number of single impurity ions in a lattice and tracing their path through the lattice, yields statistical data concerning the migration of the ions. This method is, in principle, very similar to experimental diffusion techniques

which use radio tracers. A problem is that modeling a diffusion process with an effective migration energy of more than a few electron Volts is not possible with today's computing power, due to the slow speed of the process relative to an atomic vibration. Nevertheless, it might be possible to simulate oxygen self diffusion in UO_2 (which has a relatively low activation energy), and use the results to benchmark the results obtained with the Q-H approach.

3.4 Interpretation

3.4.1 Self diffusion

Experimentally, self-diffusion coefficients are determined with a tracer method or by studying dynamics of large scale crystal defects. For instance, the self diffusion of uranium in U_3O_8 was determined [48] by applying a layer of ^{233}U onto a U_3O_8 surface and observing the penetration by measuring the gamma spectrum created by the radioactive ^{233}U. Fission product penetration is usually measured via chemical or mechanical micro-sectioning [49, 50].

The penetration as a function of time yields the diffusion coefficient. Careful experimental work is necessary to ensure which diffusion coefficient is being measured, as point defects, large scale defects such as dislocations and grain boundaries and the stoichiometry may affect the results dramatically.

Measuring diffusion coefficients at different temperatures gives us the possibility to fit equation 3.4 and obtain the Arrhenius energy, which is the sum of the migration and the defect formation energy, $\Delta H_M + E_F$ in our model.

Thus diffusion experiments can only supply us with the sum of the mechanisms underlying the diffusion process. However, by varying the stoichiometry of UO_2,

more can be learnt about E_F and ΔH_M.

3.4.2   Fission products

Fission products may diffuse through the UO_2 matrix in different ways, depending on fuel stoichiometry, irradiation conditions and fuel history. The stoichiometry (discussed later in section 4.1.3) defines the abundance of intrinsic defects through the Schottky and Frenkel disorder reactions. Irradiation acts as a source for intrinsic defects, effectively increasing the diffusion coefficient if a migration process relies on those intrinsic defects. Features such as bubbles, voids, metal segregation and precipitation can form at high temperatures after a long life in-pile and each affect the migration behaviour of fission products.

Literature concerning the release of fission products can be split into two distinct categories: in-pile and ex-pile experiments. In-pile experiments either show a high diffusion coefficient at low temperatures and linear (in Arrhenius plot) behaviour at elevated temperatures or a reduced activation enthalpy (i.e. a lower slope in the Arrhenius plot). Which of the two features are visible in an Arrhenius plot depends on the underlying mechanism controlling the fission product behaviour.

3.4.3   Interpretation of release data

Since all fission products have radioactive isotopes and can easily be detected and measured, most experiments are performed by measuring the release or the retention of fission products via γ-spectroscopy. The Booth model [51], developed to interpret release from polycrystalline materials, relates the fraction of fission product released

from a sample to the diffusion coefficient and the anneal time via:

$$F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2\pi^2 Dt/a^2). \qquad (3.5)$$

In this equation F is the released fraction, D is the diffusion coefficient, t is the anneal time and a is the equivalent sphere radius.

Equation 3.5 is an exact solution for the fraction remaining of a uniform ($t = 0$) concentration of a freely diffusing particle in a sphere with a perfect sink at the sphere surface.

Equation 3.5 is usually approximated using the following equation [7, 52]:

$$F_2(t) = 6(Dt/\pi a^2)^{\frac{1}{2}} - 3(Dt/a^2), \qquad (3.6)$$

or as $1 - F$ in case the retention is measured.

Equation 3.6 is sometimes used with only the first term. From this first term it is then concluded that diffusive release from poly-crystalline materials shows a straight line in a F - $\sqrt{t}$ plot. Figure 3.2 shows that this approximation is only valid for $F < 0.2$. When equation 3.6 is used fully, the approximation is valid for $F < 0.8$. The common conclusion that all diffusive release shows a straight line in the F - $\sqrt{t}$ plot is therefore invalid in most cases.

In UO_2 one can argue that it is reasonable that the grain boundaries might act as effective sinks, but the equation must break down if particles interact. This might not be as bad as it seems since the initial arrival at the sphere/grain surface might indeed reflect the free diffusion of nearby particles – and hence the early $[F - \sqrt{t}]$ relationship may have some validity.

Although the model is derived with a as the grain size, when it is applied, a is generally thought to be a radius larger than the grain size and smaller than the
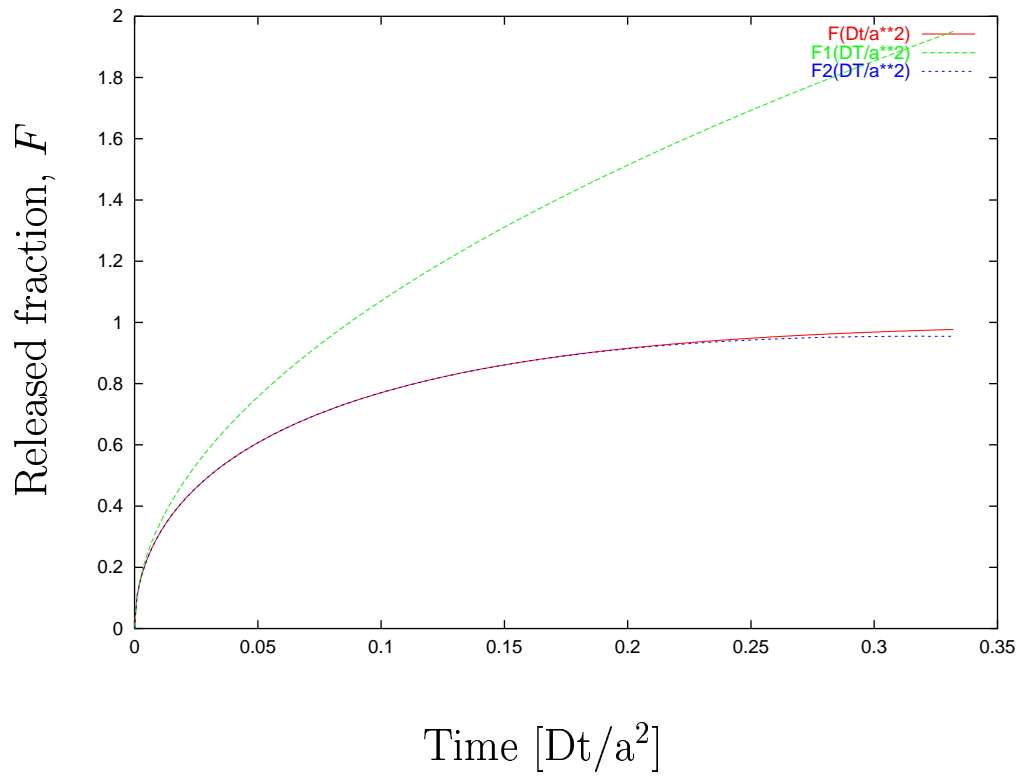
Figure 3.2: The release F of fission products as a function of Dt. The first order approximation is valid up to 20% release and the second order approximation up to 80%.

sample size [53]. Once one starts playing with and changing the value of the a parameter, the whole application of the Booth model seems flawed.

Furthermore, the Booth model assumes spherical grains which seems a reasonable model geometrically, but this fails to take into account facets with specific crystallographic orientations. Crystallographic orientation is almost certain to be an important parameter in the release of fission products from the grain into the grain boundary.