

## DEFECTS AND DIFFUSION IN METAL OXIDES

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### 1. INTRODUCTION

Mass transport by diffusion in oxides is important in many areas of materials technology; such as, fabrication (e.g. by sintering), deterioration (e.g. oxidation and corrosion) and properties (e.g. ionic conductivity and creep). In some cases it is the most mobile species that controls behaviour, as in corrosion, whereas in others, such as creep, it is the least mobile species. Investigations of diffusion in oxides usually have two objectives. The first is simply to measure the characteristic diffusion coefficient,  $D$ , and its dependence on major variables, such as temperature, pressure and composition. The second is to identify, through a suitable combination of experiments and theory, the defects which are responsible for the diffusive motion at the atomic level.

In this contribution we first summarise the theoretical background underpinning the current view of point defects and diffusion and describe some of the experimental techniques that have been used. We then consider some examples of self diffusion in binary oxides and how these may be influenced by dopants (impurities) and finally go on to explore additional complications, such as multicomponent oxides, chemical diffusion and short-circuit diffusion.

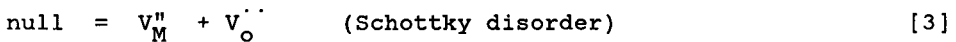
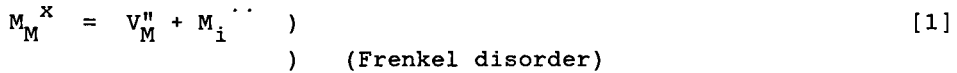
### 2. THEORETICAL BASIS

#### 2.1 Point Defects

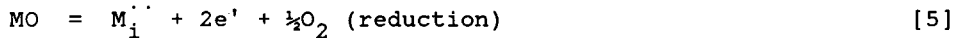
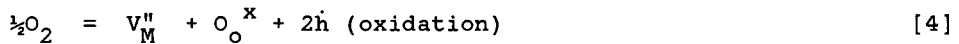
The theoretical approach to describing point defects and diffusion in oxides is adapted from that originally formulated for ionic crystals as summarised by Lidiard (1) and Kröger (2). The difference between the oxides and the truly ionic crystals is that the oxides are usually electronic semiconductors. This is incorporated into the theory by treating the electronic carriers (electrons,  $e$ , or holes,  $h$ ) as part of the defect system. A comprehensive survey of the application of these ideas to binary oxides up to 1972 has been given by Kofstad (3). The approach is

to express reactions between point defects as though they were chemical reactions. 'Mass action laws' can then be used to express relationships between the concentrations of these defects at equilibrium and the free energy changes of the defect reactions.

In oxides approaching full ionic character with ions of fixed valency (e.g. MgO) the dominant reactions tend to be those which preserve stoichiometry such as (for a binary oxide MO):



On the other hand, for oxides of ions of variable valency (e.g. transition metal oxides) oxidation/reduction reactions involving external oxygen gas tend to dominate:



In these equations the notation of Kröger and Vink has been used to specify the defects. In these reactions point defects are formed and thus the free energy change of the reaction is the free energy of formation of the defect(s),  $g_f$ . (NB In order to preserve electrical neutrality and lattice sites, defects are never created singly.) The equilibrium constant,  $K$ , for the defect-forming reaction is then related to  $g_f$  by

$$g_f = h_f - Ts_f = -k_B T \ln K \quad (6)$$

In the limit of non-interacting point defects (ideal solid solution)  $K$  may be written in terms of the defect concentration expressed as a molecular fraction (e.g.  $[V_M'']$ ). The upper limit of molecular fraction for this to be valid is probably about  $10^{-4}$ . Nevertheless, it is common practice to use this approximation at much higher concentrations (e.g. up to about  $10^{-2}$ ). This superficial success has been achieved by approximating some of the interactions between point defects in terms of the formation of associated, or complex, defects. A common example is the trapping

of an electronic defect at an oppositely charged lattice defect, such as:

$$V_M'' + h = V_M' \quad [7]$$

An alternative approach, which is not so simple in its application, is to use activities (e.g.  $\{V_M''\}$ ) instead of concentrations in the mass action equations. At low defect concentrations the defect-defect interactions can be described by an activity coefficient calculated from the Debye-Hückel theory. For example, Wagner (4) has estimated that for  $V_{Cu}'$  and  $h$  defects in  $Cu_{2-x}O$  at  $1000^\circ C$  the activity coefficient is about 0.5 when  $x = 10^{-3}$ . Since the Debye-Hückel theory assumes a continuum, it is inappropriate when defects occupy neighbouring sites. Theoretical treatments have been developed to analyse this regime, but are not convenient for routine interpretation of experimental data (5,6).

Application of the ideal mass action laws to the defect reactions, when combined with the condition for overall electrical neutrality, predicts that defect concentrations are simple power functions of oxygen activity,  $a_{O_2}$ , when redox reactions are involved:

$$[\text{defect}] \propto a_{O_2}^n \quad [8]$$

The exponent,  $n$ , is characteristic of the defect type and therefore measuring a property, such as diffusion, as a function of oxygen activity enables the defect which is responsible to be identified, or at least the range of possibilities is narrowed. The exponent  $n$  may be different for different macroscopic properties. Thus we distinguish between them as follows:

- $n_x$  for deviation from stoichiometry,
- $n_\sigma$  for electrical conductivity, and
- $n_D$  for diffusion.

In practice it is usually found that  $n_x$ ,  $n_\sigma$  and  $n_D$  are not equal and, furthermore, often vary with oxygen activity. This is an experimental manifestation of the non-ideal nature of the defects already referred to. To fit the experimental data, point defect models have become rather complicated in some cases and, furthermore, the fit is often not unique. Therefore, when

thermodynamic parameters describing these models are presented the nature of this force-fitting (i.e. assuming ideal solid solution under conditions where it is not really valid) must be borne in mind (7).

## 2.2 Diffusion

For a random walk in an isotropic lattice the tracer diffusion coefficient is given by (1)

$$D^* = \frac{1}{6} f \Gamma r^2 \quad [9]$$

where  $\Gamma$  is the jump frequency and  $r$  the jump distance.  $f$  is the correlation factor which accounts for non-random motion of the tracer and is characteristic of the lattice type and the diffusion mechanism. For a vacancy mechanism in an fcc or bcc lattice, constant  $a_o$ , then equation [9] becomes:

$$D^* = a_o^2 w_o f [V] \quad [10]$$

where  $w_o$  is the rate of exchange between a vacancy and a neighbouring ion. Hence the diffusion coefficient of the vacancy alone is

$$D_V = a_o^2 w_o . \quad [11]$$

Since the jump is thermally activated over a free energy barrier the exchange rate is related to the vibrational frequency,  $\nu$ , by

$$w_o = \nu \exp (s_m/k_B) \exp (-h_m/k_B T) \quad [12]$$

where  $s_m$  and  $h_m$  are the entropy and enthalpy of motion of the defect.

The correlation factor,  $f$ , may be used, experimentally, to aid in identifying the point defect involved in diffusion. One method of measuring  $f$  approximately is by comparing the diffusion coefficients for two isotopes ( $\alpha$  and  $\beta$ ) of the same element. For a single atom jump mechanism this gives the so-called isotope effect

$$f\Delta K = \left( \frac{D_\alpha}{D_\beta} - 1 \right) / \left( \left( \frac{M_\beta}{M_\alpha} \right)^{1/2} - 1 \right) \quad [13]$$

for a single atom jump mechanism (8).

$\Delta K$  is less than and close to unity and is also dependent on the mechanism. Although this means that  $f$  is not directly accessible, knowledge of  $f\Delta K$  is often sufficient to identify the mechanism, or distinguish between alternatives which give the same, or similar, exponents,  $n_D$ . The values of  $f\Delta K$  for different mechanisms have been summarised by LeClaire (8) and examples of its use are to be found in the studies of diffusion in transition metal oxides by Peterson and co-workers (9).

Tracer diffusion is normally studied in systems at chemical equilibrium so that the only driving force for change is the mixing of the tracers (isotopes) under their concentration gradients. When diffusion takes place in a system not at a chemical equilibrium it is known as chemical diffusion. In such a case there exist gradients of chemical activity of the oxide components that provide additional driving forces for mass transport. A typical example, which will be discussed later, is interdiffusion of two solid solutions of different initial composition. In oxides, however, there is a special case of chemical diffusion that arises because of the gaseous nature of oxygen. In order to define the thermodynamic state of an oxide the oxygen activity (partial pressure in atmospheres) must be specified. In a non-stoichiometric oxide, of general formula  $M_{1+x}O_v$ , the value of  $x$  will depend on oxygen activity (equation [8]) and therefore if the oxygen pressure is changed from one value to another a compositional change must propagate through the oxide as it adjusts to a new value for  $x$ . This is achieved by the coupled (ambipolar) diffusion of point defects (e.g. metal interstitial ions and electrons). The flux of species across a plane in the oxide ( $z = 0$ ) fixed relative to local lattice planes can be quantified in terms of a diffusion coefficient defined by

$$J_i = - D_{\text{chem}} \frac{dC_i}{dz} . \quad [14]$$

Wagner (10) has shown how  $D_{\text{chem}}$  is related to the tracer diffusion coefficient. If metal ion diffusion is more rapid than oxygen diffusion the result is

$$D_{\text{chem}} = \frac{1}{2vx} \frac{D^*(M)}{f} / \left( \left| \frac{\partial \ln x}{\partial \ln a(O_2)} \right| \right) \quad [15]$$

where  $D^*(M)$  is the tracer diffusion coefficient of the metal ion. Using equations [8] and [10], for a simple case of diffusion of cation vacancies in an oxide  $MO$ , then equation [15] reduces to

$$D_{\text{chem}} = \frac{D^*(M)}{2n_x[V]f} = \frac{D_v}{2n_x} \quad [16]$$

This result can be used to determine the vacancy diffusivity,  $D_v = a_o^2 w_o$ , or to check the expected relationship between parameters derived from other experiments.

Theoretical techniques have been developed to compute the characteristic energies of the defects describing their formation and migration. The most widely used technique is to estimate the energies by allowing atoms to relax to their lowest energy positions (except the one which is being forced to move). Since the energies are static potential energies the method has become known as 'molecular statics' and the resulting parameters are internal energies at absolute zero of temperature. These are approximately equal to enthalpies at constant pressure (i.e.  $h_f$  and  $h_m$ ). These methods have been applied extensively to oxides by Catlow (11) and Mackrodt (12). In order to estimate concentrations of defects and diffusion coefficients the techniques have been extended to permit calculation of the entropy changes,  $s_f$  and  $s_m$ . These have now been applied successfully to a few oxides (13).

An alternative approach is a 'molecular dynamics' simulation in which all the atoms are moving simultaneously. Since a 'jump' is a relatively rare event, the method can only be used to simulate high temperatures or materials in which diffusion is particularly rapid (e.g. fast ion conductors). An example of its use is the work of Gillan et al. (14).

### 3. EXPERIMENTAL TECHNIQUES

There are many diffusion-controlled phenomena from which it is possible, in principle, to deduce a diffusion coefficient. However, the most reliable technique for most diffusion coefficients has been found to be depth profiling, in which the concentration of diffusant is determined as a function of distance from a planar diffusion source.

For self-diffusion measurements an isotopic tracer of the host element is used. If, as is usually the case, this is a radioactive

isotope then the depth profile is most often determined by sectioning and counting. When diffusion distances are large the most convenient technique for sectioning is by grinding the oxide sequentially parallel to the diffusion source plane. By using careful polishing techniques it is possible to obtain a depth resolution of about 0.5  $\mu\text{m}$ , but for shallow depths of diffusion microsectioning techniques have been developed. These were first applied to diffusion in metals and have since been adapted for use with oxides. They are based on ion erosion with the source of ions being either a radio frequency plasma (15), or an ion beam source (16). A constant fraction of the sputtered material is collected on a substrate which can then be counted subsequently. Both configurations have been automated and are capable of an ultimate depth resolution of about 5 nm. The dynamic range of concentration which can be explored by a radiotracer technique can be as large as 5 or 6 decades and, even if the diffusant is an impurity, the tracer still does not dope the oxide significantly in many cases.

Unfortunately, for studies of oxides, there is no convenient radioisotope for oxygen, but there are stable isotopes  $^{17}\text{O}$  and  $^{18}\text{O}$ . In early experiments with these isotopes total exchange with  $^{16}\text{O}$  was measured as a function of time on a powdered sample. Subsequently, depth profiling techniques were developed for  $^{18}\text{O}$  based either on nuclear reaction analysis (17), or secondary ion mass spectrometry, SIMS (18). It is now generally recognised that the depth-profiling methods are more reliable than the total exchange methods. The dynamic range of useful oxygen isotope concentration is limited because of the naturally-occurring background levels of these isotopes.

For impurity diffusion it is possible to use either a radiotracer, if it is desired to keep the total concentration negligible, or the actual chemical species. For the latter it is convenient to use electron probe microanalysis (EPMA) for large penetration depths and SIMS for shallow depths.

The solutions to the diffusion equations for one-dimensional diffusion from either a finite thin source, finite thick source, or source of constant surface concentration may be found in standard texts (19). In many practical cases, however, significant deviations from ideal behaviour may be observed resulting from the assumed theoretical boundary conditions not being met. These are often evident in studies of oxygen diffusion and the basic

solutions have been modified to account for such perturbing factors as loss of material by evaporation, or gain by condensation, and a relatively slow exchange of isotopes and the source plane (20).

The chemical diffusion coefficient,  $D_{\text{chem}}$ , may be measured by monitoring the relaxation of a bulk parameter following a sudden change in oxygen activity. Electrical conductivity or mass are the parameters usually chosen (e.g. (21)). In recent years the measurement of mass changes coulometrically (using a solid electrolyte oxygen ion conductor) has become popular (22).

Diffusion data for specific oxides may be traced through bibliographies (23,24).

#### 4. SELF-DIFFUSION IN BINARY OXIDES

##### 4.1 General Comments

The extent and type of non-stoichiometry is the key factor determining the general diffusion behaviour of an oxide. In Table 1 several oxides have been classified on this basis. The non-stoichiometric formulae have been written such that  $x$  is always

TABLE 1

Non-stoichiometry in some binary oxides

Degree of Non-Stoichiometry	Cation Deficiency	Anion Deficiency
'Large'	$\text{UO}_{2+x}$ $\text{Mn}_{1-x}\text{O}$ , $\text{Fe}_{1-x}\text{O}$	$\text{UO}_{2-x}$
'Small'	$\text{Co}_{1-x}\text{O}$ , $\text{Cu}_{2-x}\text{O}$ $\text{Ni}_{1-x}\text{O}$ $\text{Fe}_{3-x}\text{O}_4$	$\text{ZrO}_{2-x}$ $\text{Fe}_2\text{O}_{3-x}$ $\text{Fe}_{3+x}\text{O}_4$
Negligible	$\text{Al}_2\text{O}_3$ , $\text{MgO}$	

a positive quantity;  $+x$  indicating interstitial defects and  $-x$ , vacancies. The approximate classification of deviation from stoichiometry is that 'large' is when the deviation exceeds about 1%, 'negligible' is when the deviation defies measurement ( $\lesssim 10^{-5}$ ) and 'small' is inbetween. It is clearly not possible in an article of this size to survey the properties of all the oxides that have been studied, or, indeed, to give illustrative examples of all



types of behaviour. Instead, the approach taken here is to discuss only a few representative examples.

#### 4.2 Fluorite Structure Oxides

This class covers such oxides as  $\text{UO}_2$ ,  $\text{ThO}_2$ ,  $\text{PuO}_2$ ,  $\text{ZrO}_2$  and related oxides, e.g.  $\text{Y}_2\text{O}_3$ . In these oxides oxygen diffuses far more rapidly than the metal cations. In the pure state they are semiconducting oxides, but are often used in the doped state when they then become efficient ionic conductors.  $\text{UO}_2$  has been studied particularly thoroughly because of its importance in nuclear power systems.

Diffusion and defects in  $\text{UO}_2$  have been summarised by Breitung (25) and Matzke (26,27). The dominant defects in oxygen rich non-stoichiometric  $\text{UO}_{2+x}$  are oxygen interstitials and compensating electron holes (similar to  $\text{U}^{5+}$  ions), but as the oxygen activity is reduced, and stoichiometry is approached, oxygen Frenkel disorder ( $\text{O}_i''$  and  $\text{V}_\text{O}^{\bullet\bullet}$ ) dominates. This results in oxygen diffusion exhibiting two activation energies (at constant  $x$ ) with the temperature of transition between the two regions being dependent on  $x$  (Figure 1). The activation energy for migration of the  $\text{O}_i''$  defect is 0.52 eV from the activation energy for oxygen tracer diffusion in the oxygen rich region. Close to stoichiometry and in the oxygen deficient region the more mobile (but more difficult to form) oxygen vacancy is responsible for diffusion.

Matzke (27) has correlated lattice diffusion of cations in  $\text{ThO}_2$ ,  $\text{UO}_2$  and  $\text{CaF}_2$  and shown that they approximate to a common behaviour as a function of reduced temperature,  $T/T_m$ .

#### 4.3 Transition Metal Oxides

The transition metal oxides display a wide variety of behaviour. Diffusion in some of these oxides ( $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{FeO}$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{NiO}$  and  $\text{Cu}_2\text{O}$ ) has recently been reviewed by Atkinson (7) and the best values for thermodynamic parameters for the point defects have been summarised.

$\text{TiO}_2$  (rutile) has generally been regarded as oxygen deficient ( $\text{TiO}_{2-x}$ ), but the weight of available evidence now seems to favour metal excess ( $\text{Ti}_{1+x}\text{O}_2$ ). Titanium diffusion takes place by an interstitialcy mechanism involving a mixture of  $\text{Ti}_i^{3\bullet}$  and  $\text{Ti}_i^{4\bullet}$  defects (the relative proportion depending on temperature and oxygen activity). The activation energy for migration of the Ti interstitial is 0.68 eV and the activation energy for titanium diffusion (at constant oxygen activity) is 2.8 eV (28). Oxygen

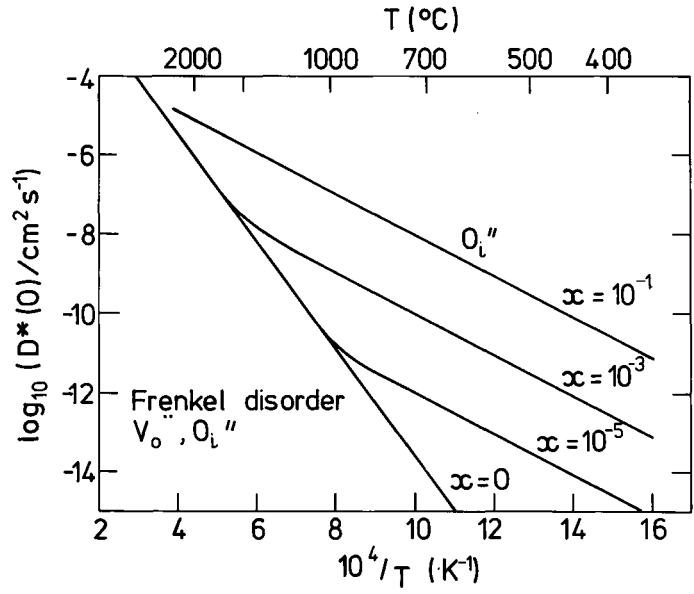


Figure 1 Oxygen tracer diffusion in  $\text{UO}_{2+x}$  (ref. 25).

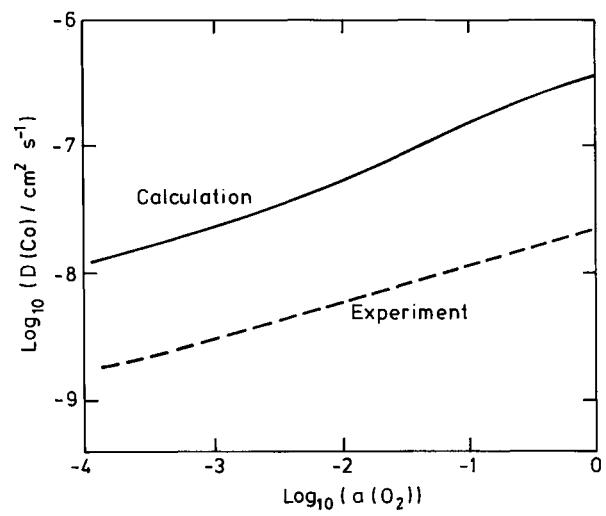


Figure 2 Cobalt diffusion in  $\text{CoO}$  at  $1200^\circ\text{C}$  as a function of oxygen activity. The calculated curve is from a static lattice simulation (ref. 30).

diffusion is much slower than titanium diffusion and probably occurs by a vacancy which has a high activation energy for migration; about 2.9 eV (29).

The rocksalt structure oxides ( $\text{NiO}$ ,  $\text{CoO}$ ,  $\text{MnO}$  and  $\text{FeO}$ ) are all cation deficient ( $\text{M}_{1-x}\text{O}$ ) with  $x$  generally increasing on going from  $\text{NiO}$  to  $\text{FeO}$ . It is well established that cation diffusion in these oxides is by a vacancy mechanism, but there is still much argument about the extent of interaction between defects, particularly at large values of  $x$ . Activation energies for cation vacancy migration in these oxides are about 1.5 eV (7) and more complex defects (where these are definitely known to exist, as in  $\text{FeO}$ ) are relatively immobile. Atomistic calculations of point defect properties are in fair accord with experimental observations in those oxides. A recent notable success has been a calculation of  $g_f$  and  $g_m$  for cation diffusion in  $\text{CoO}$  which has allowed direct calculation of the diffusion coefficient (Figure 2) and is within an order of magnitude of the measured value (30). Oxygen diffusion is extremely slow in these oxides (Figure 3) and activation energies at constant oxygen activity are large (about 5 eV). Although the oxygen lattice is a close-packed structure, both experimental and theoretical studies seem to favour oxygen diffusion by an interstitialcy mechanism (or a mixture of interstitialcy and vacancy diffusion (32,39)).

$\text{Fe}_3\text{O}_4$  (magnetite) has been particularly well-studied by Dieckmann and co-workers (40). Iron diffusion is much faster than oxygen diffusion and takes place by iron vacancies at high oxygen activity and iron interstitials at low oxygen activity. The isotope effect studies of Peterson et al. (9) are a particularly good example of their use in helping to clarify a diffusion mechanism.

$\text{Fe}_2\text{O}_3$  (hematite), on the other hand, is oxygen deficient and, on present evidence, it appears that oxygen vacancies are the dominant defects. Nevertheless, iron diffuses more rapidly than oxygen in hematite; probably by an interstitialcy mechanism. The activation energy for iron diffusion at constant oxygen activity is high (6.0 eV) even though iron is the faster diffusing species (7).

The situation in  $\text{Cr}_2\text{O}_3$  is controversial because of the very low defect concentrations in this oxide and the resulting experimental difficulties. On the balance of present evidence it appears that the dominant defects are chromium interstitials at low oxygen activity and chromium vacancies at high oxygen activity. In

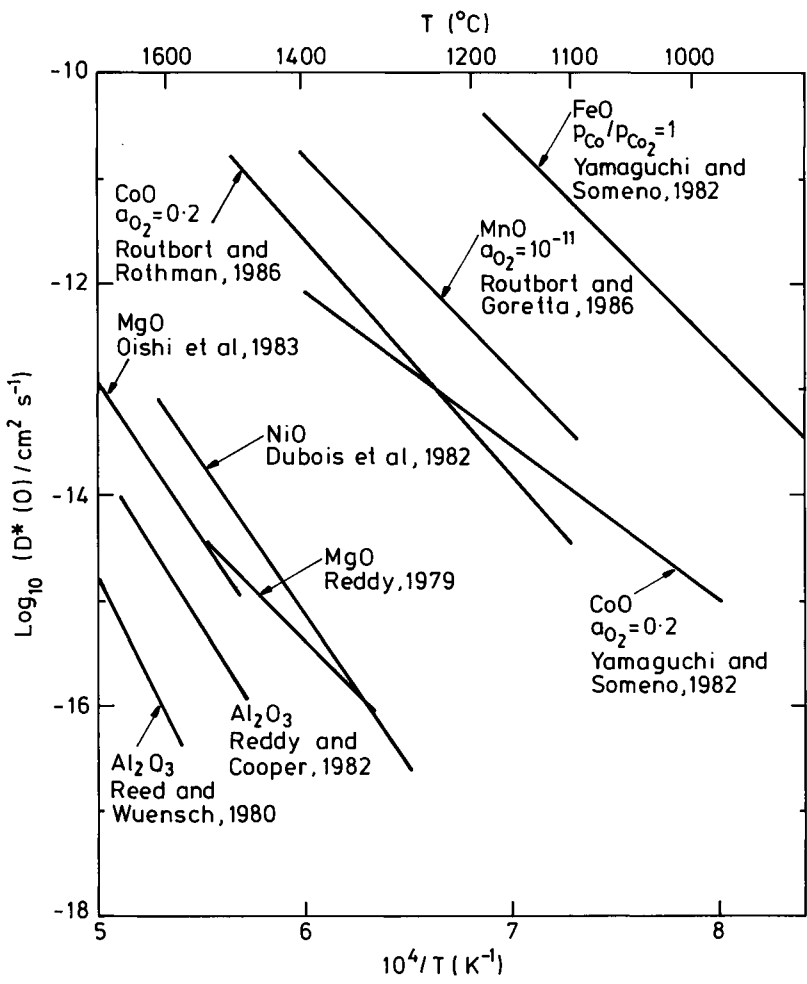


Figure 3 Oxygen tracer diffusion in some close packed oxides (refs. 31-38).

this respect it is similar to  $\text{Fe}_3\text{O}_4$ . The activation energy at constant oxygen activity for chromium diffusion in the vacancy region is high (about 6 eV (7)).

#### 4.4 Refractory Oxides $\text{Al}_2\text{O}_3$ and $\text{MgO}$

There has been a great deal of interest in these oxides over the years because of their importance as high temperature materials. Nevertheless, they remain relatively poorly understood because point defect concentrations and diffusion coefficients are extremely low (Figure 3). Indeed it is now generally accepted that no measurements in these oxides represent true intrinsic behaviour (i.e. unaffected by impurities). These difficulties have been compounded by the lack of convenient radioactive isotopes for Al and Mg.

#### 4.5 Glasses

Diffusion in amorphous oxides has been summarised by Frischat (41). The analogue of self-diffusion is diffusion of the network-forming elements. In the simplest binary oxide glass,  $\text{SiO}_2$ , these are silicon and oxygen. In silica glass the network structure may be regarded as being formed from  $\text{SiO}_4$  tetrahedral units which generate a three-dimensional network by corner-sharing the oxygen atoms. The network defects are thus departures from this network-forming rule. In this way, two oxygens bonded to each other ( $\equiv\text{Si}-\text{O}-\text{O}-\text{Si}\equiv$ ) are equivalent to a silicon vacancy and conversely  $\equiv\text{Si}-\text{Si}\equiv$  bonds are equivalent to an oxygen vacancy. Those species having unsatisfied bonding requirements (dangling bonds) are the equivalent of electronic defects. On this basis, it is possible to describe diffusion in amorphous materials in analogous terms to those used for crystalline materials even though the bonding is sufficiently covalent and directional that the ionic picture is not really appropriate.

In amorphous silica, self-diffusion of silicon is extremely slow and probably takes place by the analogue of a vacancy mechanism. The activation energy is high (Figure 4) reflecting the large number of directional bonds that have to be broken and reformed for migration to take place.

Oxygen diffusion appears to occur by two mechanisms. The silica structure is sufficiently open that an oxygen molecule can be accommodated in some parts of the network. This molecule can diffuse as a direct interstitial species with a high diffusion coefficient. In dry conditions the interstitial oxygen does not exchange readily with oxygen in the network. Consequently the two

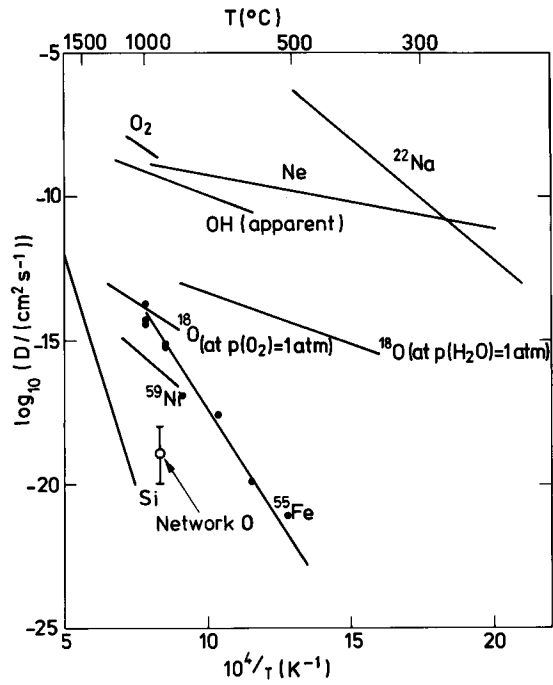


Figure 4 Diffusion of a variety of species in amorphous silica (refs. 41-47).

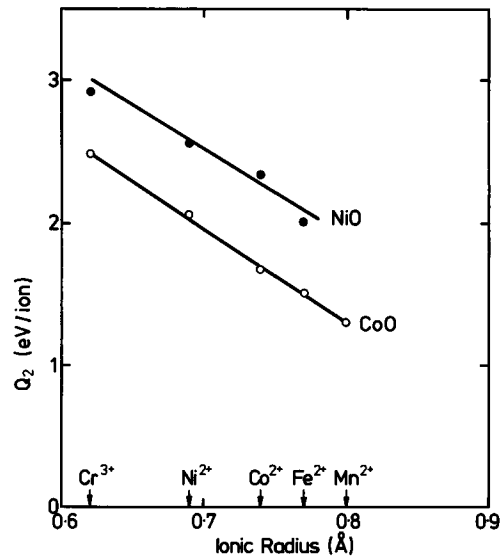


Figure 5 Activation energy for tracer soluble diffusion in NiO and CoO as a function of the ionic radius of the solute (ref. 48).

diffusion processes are independent and the tracer diffusivity of network oxygen is almost as low as that of silicon (Figure 4). In relatively small amounts of water vapour (e.g. 1-10 ppm in the gas) the exchange between interstitial oxygen and network oxygen is catalysed by -OH groups. Under these conditions the tracer diffusion coefficient is increased by several orders of magnitude. When the water vapour concentration is high (e.g. in steam at one atmosphere) interstitial water molecules themselves become the principal carriers of oxygen, rather than interstitial  $O_2$  molecules. As a consequence the 'diffusivity of oxygen' in amorphous silica covers an extremely wide range and care has to be taken in defining the exact parameter and the conditions (particularly of water vapour) under which it has been measured.

## 5. DOPANTS, IMPURITIES AND TERNARY OXIDES

### 5.1 Tracer Impurity (Solute) Diffusion

The diffusion of impurity tracers themselves (at sufficiently low concentration not to influence the native point defect concentrations) can be extremely complicated. If the impurity diffuses by the same point defect (say a vacancy) as the host, the ratio of their tracer diffusion coefficients is given by (8)

$$\frac{D_2^*}{D_O^*} = \frac{w_2}{w_O} \frac{f_2}{f_O} \cdot \exp(-h_A/k_B T) \quad [17]$$

provided that  $|h_A|$  is small enough.  $h_A$  is the energy of association between the impurity and a vacancy and is negative for an attraction between the two. In this equation the subscript 2 denotes the impurity and  $w_2$  is the jump frequency of an impurity/vacancy exchange. The correlation factor for the impurity,  $f_2$ , is a complicated function of all the jump frequencies in the vicinity of the impurity. It is approximately bounded by  $f_2(\min) \approx \frac{w_O}{w_2}$  when  $w_2 \gg w_O$  and  $f_2(\max) = 1$  when  $w_2 \ll w_O$ .

Tracer diffusion coefficients for a range of cation impurities in CoO and NiO have been reported by Hoshino and Peterson (48) and Monty (49). In general, the results (Figure 5) show a trend in which small ions diffuse more slowly than large ones and have larger activation energies for  $D_2^*$ . (There are exceptions, however, such as  $Ca^{2+}$  which is large and diffuses slowly.) Theoretical estimates of the activation energy of  $w_2$  do not reproduce this

trend for divalent impurity ions (12). In particular, the measured activation energy of  $D_2^*$  for Fe and Mn in NiO is about 0.7 eV lower than of  $D_{Ni}^*$ , whereas theory suggests they should all be the same to within 0.1 eV. Indeed, it is difficult to envisage how such low activation energies could arise for any divalent ions. This is because even if the impurity jump  $w_2$  is very fast the limiting value of  $f_2$  is approximately  $w_o/w_2$  and hence  $D_2/D_o$  has the limiting value  $\exp(-h_A/k_B T)$ . Physically, this corresponds to the impurity repeatedly exchanging with the same vacancy. A low activation energy can thus only occur if  $h_A$  is appreciable and negative (in this case about -0.7 eV). This could be explained if Fe and Mn are present as trivalent ions in NiO at low concentrations.

The trend for diffusivity to increase as ionic size increased found in CoO and NiO is not repeated in MgO. Wuensch (50) has carried out a similar survey for divalent solute ions in MgO and has found the opposite correlation in that the smaller the ion the larger is its diffusivity (Figure 6). There is, nevertheless, general agreement that higher valency cations in these oxides diffuse more slowly. Since a trivalent impurity cation will be attracted to a divalent vacancy,  $V_M''$ , the association energy,  $h_A$ , will be large and negative (about -1 eV). This contribution tends to make the impurity diffuse faster than the host since vacancies are preferentially attracted to the impurity. However, the opposite is found in reality and this implies that  $w_2 \ll w_o$  for impurities of greater charge. The lowering of the jump frequency is probably because the coulombic contribution to the energy at the saddle point of the jump (the activation energy) increases as the charge on the jumping ion increases.

## 5.2 The Effect of Doping on Diffusion

The effect of dopants on diffusion is complicated in that there are two broad types of dopant; homovalent and heterovalent; and two types of diffusion; self-diffusion and impurity diffusion.

The effects of homovalent cation substitutional dopants on diffusion have been studied extensively in the rocksalt-structured oxides NiO, CoO, FeO and MgO. The cations are sufficiently similar in size that these oxides form complete ranges of solid solution. It is found (51) that the influence of the homovalent dopant on self-diffusion of the host cation is small, unless the concentration of the dopant is large. The main effect is on the energy of formation,  $h_f$ , of the cation vacancy responsible for



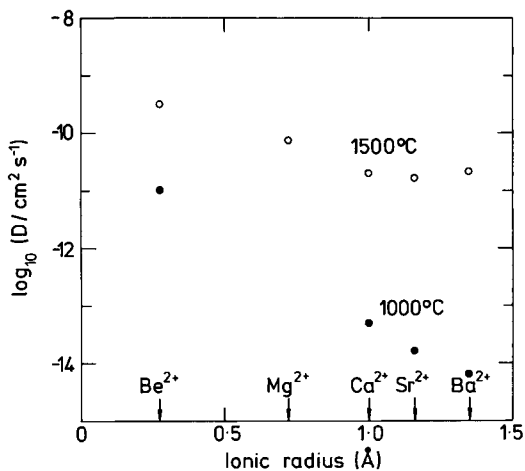


Figure 6 Diffusion of solute ions in MgO as a function of the ionic radius of the solute (ref. 50).

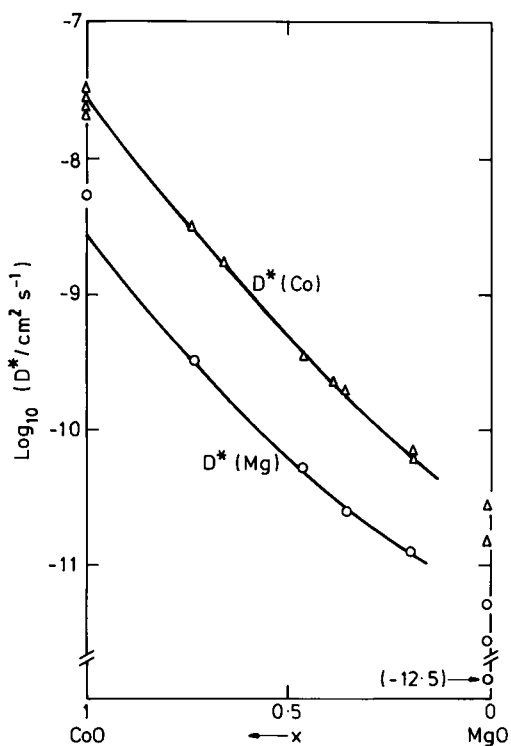


Figure 7 Diffusion of Co and Mg in mixed crystals of  $\text{Co}_x\text{Mg}_{1-x}\text{O}$  at 1300°C (ref. 52)

diffusion which varies linearly between the two end members of the solid solution, i.e.

$$h_f = (1-x) h_{f0} + x h_{f2} \quad [18]$$

where 0 and 2 are the host and dopant and  $x$  is the cation fraction of dopant. This leads to an activation energy which varies linearly with composition. A typical example is Mg doping of CoO (Figure 7) where the Mg reduces the diffusion coefficient of Co because it is more difficult to form cation vacancies in MgO than in CoO (52).

Extensive solid solution is only possible when the ions are similar in size. If the ionic sizes are very different then the solid solution is correspondingly limited and stronger interactions are generated between the dopant and defects on the host lattice. For example, if the dopant is larger than the host it will tend to attract host vacancies to minimise the strain associated with the size mismatch. This attractive interaction can be described by a binding energy between the dopant and the host vacancy. If the dopant is also relatively immobile then the dopant acts as a trap for host vacancies and would thereby be expected to reduce diffusion of the host cation. Typical values for the binding energy between defects due to size mismatch are up to 0.5 eV (12).

In oxides, which are mainly ionically bonded materials, heterovalent dopants carry an effective charge with respect to the host lattice and therefore must be compensated electrically by defects with an opposite effective charge. A typical example is a trivalent dopant, such as Al, in an oxide of a divalent cation, such as NiO. For this particular example one nickel vacancy (with an effective double negative charge) will be created for every two aluminium dopant ions (with effective single positive charge). According to this simple picture the concentration of vacancies is one half the concentration of dopant and the activation energy for Ni diffusion should be the enthalpy of vacancy motion,  $h_m$ . Experimental measurements (53) of Ni diffusion in Al-doped NiO have shown that this is not the case. The reason is that the oppositely charged defects have an attractive interaction which binds them together in the same kind of way as described earlier for homovalent oversize dopants. The coulombic interaction between the charged defects is, however, stronger than the strain interaction and hence the binding energy tends to be greater; up to about

1.0 eV. At sufficiently low temperature, or sufficiently high doping, pairs of defects will interact to form larger agglomerates and lead eventually to nucleation and precipitation of a second bulk phase; in this case the spinel,  $\text{NiAl}_2\text{O}_4$ . It should be emphasised that these interaction energies are such that most of the defects are bound in pairs, or larger groups, even at  $1200^\circ\text{C}$  and a doping level of about 0.5% (as cation fraction).

Reddy and Cooper (37) used crystals of  $\text{Al}_2\text{O}_3$  doped with either 100 ppm (by weight) of  $\text{MgO}$  or 800 ppm  $\text{TiO}_2$  plus 300 ppm  $\text{Cr}_2\text{O}_3$  to try and determine the mechanism of oxygen diffusion. They found that Mg doping had no effect, but that Ti doping lowered  $D_0^*$  by about a factor of 5, independent of temperature. Their explanation of these observations is that the defect structure in the undoped material is controlled by Si impurities being electrically compensated by aluminium vacancies. If the Ti dopant enters the lattice as a  $\text{Ti}_{\text{Al}}$  defect it will increase  $[\text{V}_{\text{Al}}']$  and decrease  $[\text{V}_{\text{O}}'']$  through the Schottky equilibrium. Thus they conclude that oxygen diffusion is probably by a vacancy mechanism. The lack of an effect on Mg doping (which should enter as  $\text{Mg}_{\text{Al}}'$  and have the opposite effect to Ti) is, they suggest, due to spinel precipitation.

Ando et al. (54) have employed a similar approach in studying oxygen diffusion in  $\text{MgO}$  doped with up to 1.3% by weight of Fe. They observed the doping to have very little effect at all temperatures of measurement. On the basis of the simple interpretation that the dopant defect is  $\text{Fe}_{\text{Mg}}$  these experiments appear to show that oxygen diffusion is not by a mechanism involving a charged defect (vacancy or interstitial). However, in view of the demonstrated dangers of the simple interpretation this conclusion may not be valid. It would appear that doping experiments give more information about the dopant and its interactions than they give about the host lattice.

When the solute is present as a significant dopant as well as a diffusing tracer, the interpretation is more complicated because of the influence of the dopant on the point defect concentrations. This is particularly marked for solutes with an effective charge, such as Cr in  $\text{NiO}$  or  $\text{MgO}$ . Measurements of Cr tracer diffusion in Cr-doped  $\text{MgO}$  have been reported by Weber et al. (55) and analysed in terms of Lidiard's association description of diffusion (1).

Since the Cr tracer can only move when a vacancy is associated with it on a neighbouring site, the diffusion coefficient is given by:

$$D^*(\text{Cr}) = D_c p \quad [19]$$

where  $p$  is the fraction of solute associated into complexes and is proportional to solute concentration,  $[\text{Cr}]$ , when  $[\text{Cr}]$  is small.  $D_c$  is the diffusion coefficient of the complex and is a function of the jump frequencies of the defects. For this particular example the theory predicts

$$D_{\text{Cr}}^* = 0.5 a^2 w_2 [\text{Cr}] \exp(-h_A/k_B T) . \quad [20]$$

Weber et al. confirmed that  $D_{\text{Cr}}^*$  is proportional to  $[\text{Cr}]$  and deduced that the activation energy for  $w_2$  is 1.73 eV and  $h_A$  is - 0.9 eV.

### 5.3 Ternary Oxides

Strictly speaking an impurity or dopant in a binary oxide should be regarded as a ternary system, but the term is usually reserved for mixed oxides having a well-defined stoichiometric ideal composition such as  $\text{MgAl}_2\text{O}_4$ ,  $\text{NiCr}_2\text{O}_4$ ,  $\text{BaTiO}_3$ , etc. (56). There have been few recent diffusion studies, but early experimental data for some ternary oxides were summarised by Birchenall (57). Although early data should be viewed with some caution (in some oxides later studies have revealed that earlier work was unreliable because of poor sample quality) Birchenall's review does allow certain trends to be identified. The main trend is that, not surprisingly, diffusion behaviour tends to be intermediate between that of the two binary oxides in those oxides with a close-packed oxygen lattice.

The high temperature superconductors are ternary oxides which are currently of great interest. In these materials oxygen diffusion is much more rapid than cation diffusion because of the relatively large concentration of vacancies on the oxygen sublattice. Oxygen tracer diffusion studies are now emerging for these important materials (Figure 8) and are already revealing complex behaviour (58,59,60).

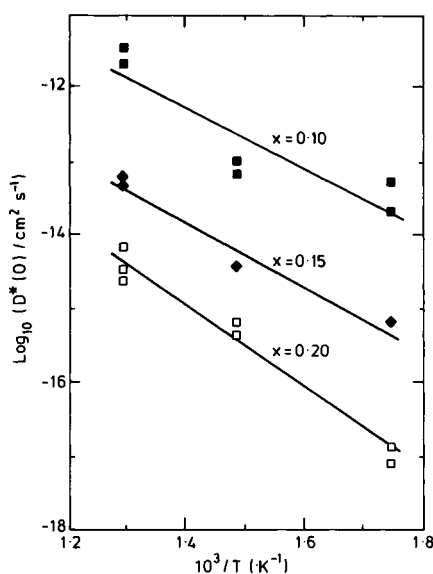


Figure 8 Oxygen tracer diffusion in the superconductor  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$  (ref. 60).

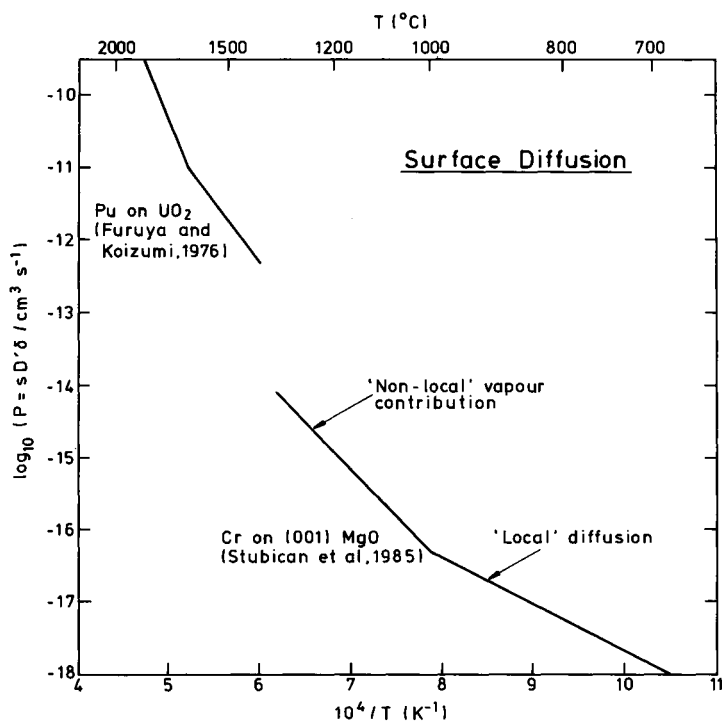


Figure 9 Surface diffusion of Pu on  $\text{UO}_2$  and Cr on  $\text{MgO}$  (refs. 71 and 72).

## 6. OTHER TYPES OF DIFFUSION

### 6.1 Interdiffusion

Interdiffusion experiments in which, for example, two cations A and B move in opposite directions to homogenise an initial discontinuity in composition are much more difficult to analyse. For the simplest case when A and B have the same valency and the anions are not mobile then the interdiffusion coefficient is given by (61):

$$D_{AB} = \frac{D_A^* D_B^*}{[A] D_A^* + [B] D_B^*} \cdot \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln [B]}\right) \quad [21]$$

where  $\gamma_B$  is the activity coefficient of B in the solution. Lindström has analysed interdiffusion in (Co, Ni)O in this way (62). The interdiffusion of metal ions of different valency on a rigid anion lattice has been measured for Cr in NiO (63) and MgO (64) and for Al in NiO (65). Lidiard's association method was used to analyse the results and to predict (66) that, for low concentrations of B,  $D_{AB} \approx 2 D_B^*$  if the complexes are associates of two defects and  $3 D_B^*$  if they contain 3 defects. Thus it was established (64) that Cr diffusion in MgO is by a  $(Cr_{Mg}^{\cdot} V_{Mg}^{\cdot\cdot})$  complex. Osenbach et al. (66) have also demonstrated the theoretical equivalence of the association method and equation [21]. When defects are mobile on both the anion and cation sublattices the analysis is even more complicated and Speight (67) has proposed a method of dealing with such a situation and applied it to the interdiffusion of Ca and Zr in calcia-stabilised  $ZrO_2$ .

### 6.2 Short Circuit Diffusion

Potential pathways for fast diffusion which can effectively short-circuit diffusion through the lattice are dislocations, grain boundaries and free surfaces. The dislocation or grain boundary is usually treated as a localised region (either a pipe or slab) in which the diffusion coefficient,  $D'$ , is greater than in the surrounding lattice. In most grain boundary diffusion experiments the parameter obtained is the product  $D'\delta$  where  $\delta$  is the effective width of the boundary slab. For isolated dislocations the corresponding parameter is  $D'd^2$ , where  $d$  is the diameter of the

dislocation pipe. From a combination of experiments having different times of diffusion it is possible to separate  $D'$  from  $\delta$  and  $d$ .

Such measurements have been made for Ni diffusion in NiO (68,69). They show that  $\delta$  and  $d$  are  $\sim 1$  nm and that previous assertions of very wide boundaries ( $\sim$  microns) in oxides are unfounded. Measurements were also made as a function of departure from stoichiometry in the lattice (i.e. as a function of  $a(\text{O}_2)$ ) and suggest that grain boundary and dislocation diffusion in NiO both take place via Ni vacancies which segregate to the boundary or dislocation. Similar experiments have shown that oxygen diffuses as an interstitial oxygen atom both in the bulk and in grain boundaries of cuprous oxide (70). Thus it would appear that grain boundary diffusion involves similar defects to those responsible for bulk lattice diffusion.

Surface diffusion on refractory oxides has been studied using tracer techniques by Stubican et al. (71) and their data for Cr on the (001) surface of MgO are presented in Figure 9. The diffusion data show clear evidence of two activation energies.

Also shown in Figure 9 are data for Pu diffusion on  $\text{UO}_2$  surfaces measured using a surface spreading technique (72). Matzke (27) has reviewed bulk diffusion data for  $\text{UO}_2$  and it is clear that the wrong bulk diffusivities were used in interpreting the surface diffusion studies. Nevertheless the break in activation energy is probably not sensitive to these effects and has also been reported by Zhou and Olander (73). The current view of the two activation energies for surface diffusion is that at low temperatures the low activation energy corresponds to diffusion by a defect mechanism (similar to solid state diffusion) in which the hopping distance is of the order of the nearest neighbour separation. At higher temperatures a non-local mechanism is invoked in which the "jump" distance is much larger, but which requires more energy to excite species almost to become a vapour (hence the large activation energy).

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