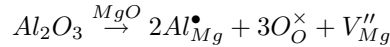


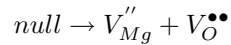
November 7, 2003

We are looking at the incorporation of  $\text{Al}_2\text{O}_3$  into  $\text{MgO}$ . Let's first start by writing the incorporation reaction as follows:



Note that this is just one possible reaction. There are many other ways you could incorporate alumina into magnesia, creating different types of defects in each case.

Now we need some real data to figure out which type of defect is most common in  $\text{MgO}$ . According to Physical Ceramics by Chiang, et. al. the dominant defects in  $\text{MgO}$  are Schottky defects. The reaction for the formation of Schottky defects is:



with a corresponding equilibrium relationship:

$$K_{eq} = [V_{\text{Mg}}''] [V_{\text{O}}^{\bullet\bullet}] = \exp\left(\frac{-G_S^f}{kT}\right)$$

We now have to account for charge neutrality, taking into consideration both the extrinsic defects (namely the impurities) and the intrinsic Schottky defects.

$$2 [V_{\text{Mg}}''] = 2 [V_{\text{O}}^{\bullet\bullet}] + [\text{Al}_{\text{Mg}}^{\bullet}]$$

Here is where I made the error. The more interesting case is to look at how the cation vacancy concentration depends on the impurity levels and temperature. However, in class I continued on from this point looking at the anion vacancies. My analysis was incorrect and will now present both solutions correctly.

## 1 Cation Vacancy

For the cation vacancy concentration, namely  $[V_{\text{Mg}}'']$ , we can use the neutrality condition to get:

$$K_{eq} = [V_{\text{Mg}}''] \left( [V_{\text{Mg}}''] - \frac{1}{2} [\text{Al}_{\text{Mg}}^{\bullet}] \right)$$

$$[V_{\text{Mg}}'']^2 - \frac{1}{2} [V_{\text{Mg}}''] [\text{Al}_{\text{Mg}}^{\bullet}] - K_{eq} = 0$$

We can now solve this quadratic equation for  $[V_{\text{Mg}}'']$  yielding:

$$[V_{Mg}'' ] = \frac{1}{4} [Al_{Mg}^{\bullet}] + \frac{1}{4} \sqrt{[Al_{Mg}^{\bullet}]^2 + 16K_{eq}}$$

This relationship gives us  $[V_{Mg}'' ]$  but the term  $K_{eq}$  can be rewritten to give us a better physical understanding of the solution. Since we know in PURE MgO (with only Schottky defects), the following is true:

$$K_{eq} = [V_{Mg}'' ] [V_O^{\bullet\bullet}]$$

And from charge neutrality in the pure crystal:

$$[V_{Mg}'' ] = [V_O^{\bullet\bullet}]$$

Thus,

$$K_{eq} = [V_{Mg}'' ]_{pure}^2$$

Now we have a relation that relates  $K_{eq}$  to something more physical (the cation vacancy concentration in the pure crystal). We now go back to our original problem and get:

$$[V_{Mg}'' ] = \frac{1}{4} [Al_{Mg}^{\bullet}] + \frac{1}{4} \sqrt{[Al_{Mg}^{\bullet}]^2 + 16 [V_{Mg}'' ]_{pure}^2}$$

From this we can look at the different temperature regimes to understand variation in  $[V_{Mg}'' ]$ .

$$\begin{array}{l} \text{High Temperature} \quad [V_{Mg}'' ]_{pure} \gg [Al_{Mg}^{\bullet}] \quad [V_{Mg}'' ] \approx [V_{Mg}'' ]_{pure} \\ \text{Low Temperature} \quad [V_{Mg}'' ]_{pure} \ll [Al_{Mg}^{\bullet}] \quad [V_{Mg}'' ] \approx \frac{1}{2} [Al_{Mg}^{\bullet}] \end{array}$$

So at high temperatures the cation vacancy concentration is dominated by the intrinsic Schottky defects and at low temperatures its dominated by the vacancy creation from the impurity addition.

## 2 Anion Vacancy

Now let us consider the case of the anion vacancies which I attempted to do in recitation. We can start with the same two tools, the Schottky equilibrium statement and charge neutrality.

$$K_{eq} = [V_{Mg}'' ] [V_O^{\bullet\bullet}]$$

$$2 [V_{Mg}'' ] = 2 [V_O^{\bullet\bullet}] + [Al_{Mg}^{\bullet}]$$

This time we will solve for  $[V_O^{\bullet\bullet}]$ .

$$K_{eq} = \left( [V_O^{\bullet\bullet}] + \frac{1}{2} [Al_{Mg}^{\bullet}] \right) [V_O^{\bullet\bullet}]$$

$$[V_{O^{\bullet\bullet}}]^2 + \frac{1}{2} [Al_{Mg}^{\bullet}] [V_{O^{\bullet\bullet}}] - K_{eq} = 0$$

Solving this equation for  $[V_{O^{\bullet\bullet}}]$  yields (this is where I made the error):

$$[V_{O^{\bullet\bullet}}] = -\frac{1}{4} [Al_{Mg}^{\bullet}] + \frac{1}{4} \sqrt{[Al_{Mg}^{\bullet}]^2 + 16K_{eq}}$$

Using the same a similar substitution as in the previous case, we can eliminate  $K_{eq}$  ( $K_{eq} = [V_{O^{\bullet\bullet}}]_{pure}^2$ ).

$$[V_{O^{\bullet\bullet}}] = -\frac{1}{4} [Al_{Mg}^{\bullet}] + \frac{1}{4} \sqrt{[Al_{Mg}^{\bullet}]^2 + 16 [V_{O^{\bullet\bullet}}]_{pure}^2}$$

Again, let's look at the limits at high and low temperature:

$$\begin{array}{ll} \text{High Temperature} & [V_{O^{\bullet\bullet}}]_{pure}^2 \gg [Al_{Mg}^{\bullet}] \quad [V_{O^{\bullet\bullet}}] \approx [V_{O^{\bullet\bullet}}]_{pure} \\ \text{Low Temperature} & [V_{O^{\bullet\bullet}}]_{pure}^2 \ll [Al_{Mg}^{\bullet}] \quad [V_{O^{\bullet\bullet}}] \approx 0 \end{array}$$

This makes sense since at low temperatures there are very few intrinsic defects and the only contributions to the concentration of anion vacancies can come from the incorporation of the impurity. However, no oxygen vacancies are created when alumina is added.

Please come see me if this explanation is not clear. Again I would like to thank those people who brought this error to my attention and I am very sorry for any confusion my mistakes might have caused.

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**5.2** Find an expression for the steady-state concentration profile during the radial diffusion of a diffusant through a cylindrical shell of thickness,  $\Delta R$ , and inner radius,  $R^{\text{in}}$ , in which the diffusivity is a function of radius  $D(r)$ . The boundary conditions are  $c(r = R^{\text{in}}) = c^{\text{in}}$  and  $c(r = R^{\text{in}} + \Delta R) = c^{\text{out}}$ .

*Solution.* The gradient operator in cylindrical coordinates is

$$\nabla = \frac{\partial}{\partial r} \hat{e}_r + \frac{1}{r} \frac{\partial}{\partial \theta} \hat{e}_\theta + \frac{\partial}{\partial z} \hat{e}_z \quad (5.82)$$

The divergence of a flux  $\vec{J}$  in cylindrical coordinates is

$$\nabla \cdot \vec{J} = \frac{1}{r} \frac{\partial(rJ_r)}{\partial r} + \frac{1}{r} \frac{\partial J_\theta}{\partial \theta} + \frac{\partial J_z}{\partial z} \quad (5.83)$$

Therefore, the steady-state, radially symmetric, diffusion equation becomes

$$0 = \frac{\partial}{\partial r} \left( rD(r) \frac{\partial c}{\partial r} \right) \quad (5.84)$$

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which can be integrated twice to give

$$c(r) = c^{\text{in}} + a_1 \int_{R^{\text{in}}}^r \frac{d\rho}{\rho D(\rho)} \quad (5.85)$$

The integration constant  $a_1$  is determined by the boundary condition at  $R^{\text{in}} + \Delta R$ :

$$a_1 = \frac{c^{\text{out}} - c^{\text{in}}}{\int_{R^{\text{in}}}^{R^{\text{in}} + \Delta R} \frac{d\rho}{\rho D(\rho)}} \quad (5.86)$$

**5.3** Find the steady-state concentration profile during the radial diffusion of a diffusant through a bilayer cylindrical shell of inner radius,  $R^{\text{in}}$ , where each layer has thickness  $\Delta R/2$  and the constant diffusivities in the inner and outer layers are  $D^{\text{in}}$  and  $D^{\text{out}}$ . The boundary conditions are  $c(r = R^{\text{in}}) = c^{\text{in}}$  and  $c(r = R^{\text{in}} + \Delta R) = c^{\text{out}}$ . Will the total diffusion current through the cylinder be the same if the materials which make up the inner and outer shells are exchanged? Assume that the concentration of the diffusant is the same in the inner and outer layers at the bilayer interface.

**Solution.** The concentration profile at the bilayer interface will not have continuous derivatives. Break the problem up into separate diffusion problems in each layer and then impose the continuity of flux at the interface. Let the concentration at the bilayer interface be  $c^{i/o}$ .

Inner region:  $R^{\text{in}} \leq r \leq R^{\text{in}} + \frac{\Delta R}{2}$

Using Eq. 5.86,

$$c^{\text{in}}(r) = \frac{c^{i/o} - c^{\text{in}}}{\ln\left(\frac{R^{\text{in}} + \Delta R/2}{R^{\text{in}}}\right)} \ln \frac{r}{R^{\text{in}}} + c^{\text{in}} \quad (5.87)$$

The flux at the bilayer interface is

$$J^{i/o} = -D^{\text{in}} \frac{c^{i/o} - c^{\text{in}}}{\ln\left(\frac{R^{\text{in}} + \Delta R/2}{R^{\text{in}}}\right)} \frac{1}{R^{\text{in}} + \Delta R/2} \quad (5.88)$$

Outer region:  $R^{\text{in}} + \frac{\Delta R}{2} \leq r \leq R^{\text{in}} + \Delta R$

$$c^{\text{out}}(r) = \frac{c^{\text{out}} - c^{i/o}}{\ln\left(\frac{R^{\text{in}} + \Delta R}{R^{\text{in}} + \Delta R/2}\right)} \ln \frac{r}{R^{\text{in}} + \Delta R/2} + c^{i/o}; \quad (5.89)$$

The flux at the bilayer interface is

$$J^{i/o} = -D^{\text{out}} \frac{c^{\text{out}} - c^{i/o}}{\ln\left(\frac{R^{\text{in}} + \Delta R}{R^{\text{in}} + \Delta R/2}\right)} \frac{1}{R^{\text{in}} + \Delta R/2} \quad (5.90)$$

Setting the fluxes at the interfaces equal and solving for  $c^{i/o}$ :

$$c^{i/o} = \frac{\alpha^{\text{out}} c^{\text{out}} + \alpha^{\text{in}} c^{\text{in}}}{\alpha^{\text{out}} + \alpha^{\text{in}}} \quad (5.91)$$

where

$$\alpha^{\text{out}} \equiv \frac{D^{\text{out}}}{\ln\left(\frac{R^{\text{in}} + \Delta R}{R^{\text{in}} + \Delta R/2}\right)}; \quad \alpha^{\text{in}} \equiv \frac{D^{\text{in}}}{\ln\left(\frac{R^{\text{in}} + \Delta R/2}{R^{\text{in}}}\right)} \quad (5.92)$$

Putting Eq. 5.91 into Eqs. 5.87 and 5.89 yields the concentration profile of the whole cylinder.

The total current diffusing through the cylinder (per unit length) is

$$I = 2\pi \left( R^{\text{in}} + \frac{\Delta R}{2} \right) J^{\text{i/o}} = -\frac{2\pi D^{\text{in}} (c^{\text{i/o}} - c^{\text{in}})}{\ln\left(\frac{R^{\text{in}} + \Delta R/2}{R^{\text{in}}}\right)} \quad (5.93)$$

Using Eq. 5.91,

$$c^{\text{i/o}} - c^{\text{in}} = \frac{\alpha^{\text{out}} (c^{\text{out}} - c^{\text{in}})}{\alpha^{\text{out}} + \alpha^{\text{in}}} \quad (5.94)$$

If everything is kept constant except  $D^{\text{in}}$  and  $D^{\text{out}}$ , use of Eq. 5.94 in Eq. 5.93 shows that

$$I \propto \frac{D^{\text{in}} D^{\text{out}}}{\alpha_1 D^{\text{out}} + \alpha_2 D^{\text{in}}} \quad (5.95)$$

where  $\alpha_1$  and  $\alpha_2$  are constants. Clearly,  $I$  will be different if the materials making up the inner and outer shells are exchanged and the values of  $D^{\text{out}}$  and  $D^{\text{in}}$  are therefore exchanged. This contrasts with the result for the two adjoining flat slabs in Exercise 5.1.