0601G: The Arrhenius Equation

09/28/21: Practice HW on the topic of the Arrhenius Equation

1.

Data for the diffusion of Zr^{4+} and O^{2-} ions in the lattice and the grain boundaries are given in the last two pages of this homework (they draw from the notes which are also posted online).

Pick the temperature of 1200 °C.

(i) Give the ratio of the lattice diffusion for the (cations) Zr^{4+} to the lattice diffusion of anions at the above temperature.

(ii) Give the ratio of the boundary diffusion for the Zr^{4+} to the boundary diffusion of anions at the above temperature.

(iii) Give the ratio of the lattice diffusion for the (cations) Zr^{4+} to the boundary diffusion of cations at the above temperature.

(iv) Give the ratio of the lattice diffusion for the (anions) O^{2-} to the boundary diffusion of anions at the above temperature.

•Present all your results neatly in a table

•Then briefly discuss the significant of the results in the table in terms of the sintering process.

2.

Consider the first graph which gives the diffusion coefficients for the cations in the grain boundary and the lattice.

From the data calculate the activation energy for lattice and grain boundary diffusion and compare your results with the numbers given within the figure.

3.

Sintering occurs by mass transport from the grain boundaries into the adjacent pores.

Mass transport can occur by both boundary and volume (or lattice) diffusion.

The time for sintering by boundary diffusion was derived to be given by

$$t_S = \frac{1}{450}\frac{k_B T d^4}{\delta_{gb} D_{gb} \gamma_S \Omega}$$

The equation for sintering by lattice or volume diffusion is given by

$$t_S = \frac{1}{132}\frac{k_B T d^4}{\left(dD_{vol}\right)\gamma_S \Omega} \quad or \; = \frac{1}{132}\frac{k_B T d^3}{\left(D_{vol}\right)\gamma_S \Omega}$$

Note that the width of the boundary in the former equation is now replaced by the grain size.

Note that the grain size dependence of the time for sintering now changes from the fourth power to the third power.

Can you give an argument for replacing the boundary width by the grain size (or some factor thereof) for the volume diffusion sintering equation?

Hint: the answer lies in considering the cross section for diffusional transport from the grain boundaries into the adjacent pores.

Grain boundary an lattice diffusion of cations (Zr^{4+}) in zirconia

Taylor, Kilo, Borchardt, Weber and Scherrer
JECS: 2005; 1591-1595

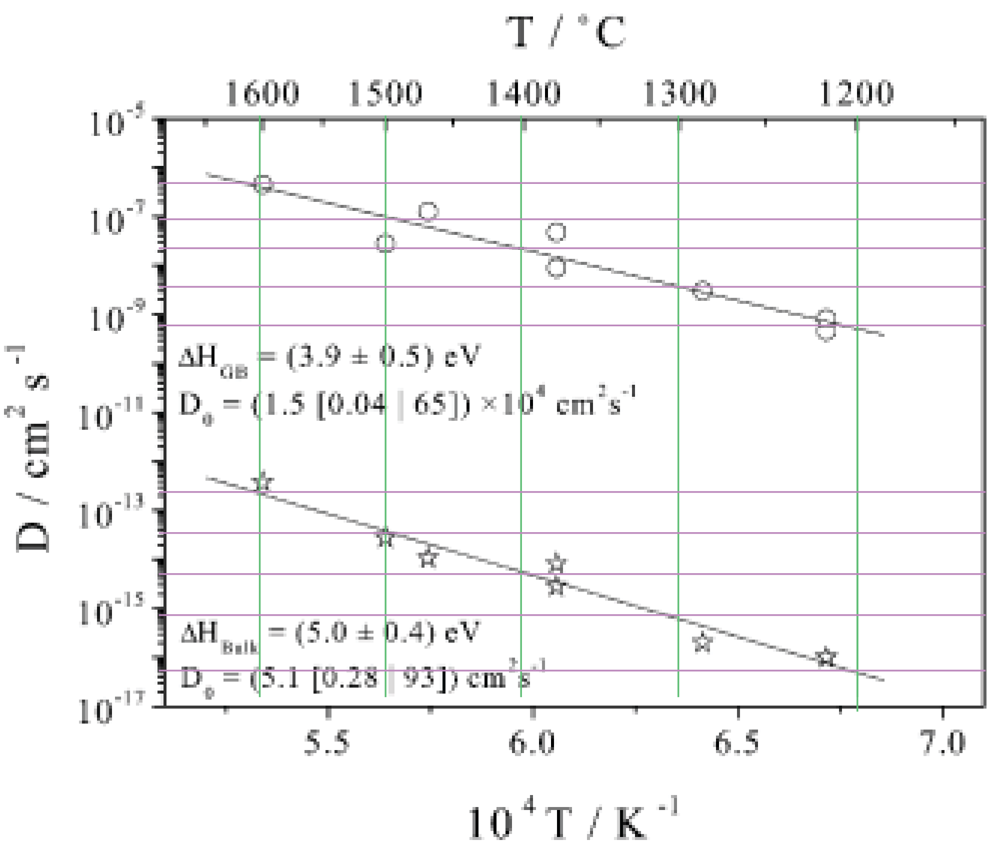

Fig. 3. Temperature dependency of ^{96}Zr tracer diffusivities. Symbols correspond to bulk diffusion (☆), and grain boundary diffusion (○), respectively.

Notes:

(i) Grain boundary diffusivity is for to five orders of magnitude higher than lattice diffusion.

(ii) The activation energy of lattice diffusion is greater. Note a more steep change in the coefficient of diffusion in the lattice than in the grain boundary.

Grain boundary an lattice diffusion of anions (O^{2-}) in zirconia

2003, Kilo, Argirusis, Borchardt and Jackson

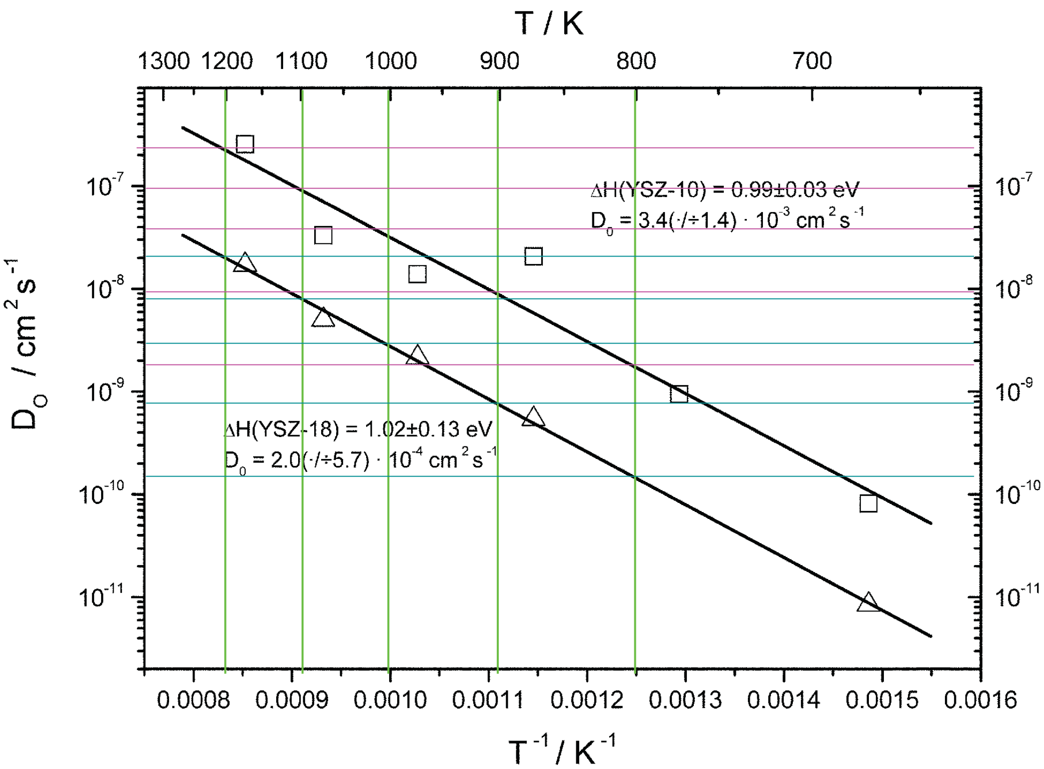

Fig. 2 Arrhenius plot of experimental oxygen diffusivities in YSZ-10 (squares) and YSZ-18 (triangles). The corresponding activation enthalpies and pre-exponential factors are included into the plot.

Notes:

(i) Note the the much higher diffusivities of oxygen ions than of the zirconium ions, both in the boundary and in the lattice.

(2) Grain boundary diffusion is faster than lattice diffusion of oxygen ions.

(3) Again note that the diffusivities vary more strongly with temperature for lattice diffusion that for boundary diffusion because of the higher activation energy for lattice diffusion.