

HW Exam on Sintering (due Wednesday Oct 13, 2021)

(Each question carries equal weight. Best if you give you your answers in paper form to me in-person, at the end of the class on Wednesday).

1: Linear Shrinkage Strain, Volumetric Strain, and Green Density

The objective of this problem is to obtain a relationship between the green density and the linear strain if the specimen sinters to full density.

Sintering is a phenomenon of large strains so that the linear strain must be defined as

$$\varepsilon = \ln \frac{L}{L_o}$$

where L_o is the initial length and L is the length as the sample shrinks.

(i) Show that ε is a negative quantity.

(ii) Then show that the volumetric strain is given by

$$\varepsilon_v = 3\varepsilon$$

(iii) Now obtain an equation that relates the green density, ρ_g , and the final density of the specimen, ρ_f , to the volumetric strain.

(iv) Assume that the specimen achieves full density at the end of the sintering process that is $\rho_f = 1$. The green density of specimens in sintering experiments can range from 0.5 to 0.6. Make a graph of the linear strain at full density, as a function of the green density.

2: Relationship between the pore radius and the relative density

In a sintering experiment the volume of the specimen decreases, but the mass of the specimen remains constant.

The grains are assumed to be in the shape of cubes while the pores are assumed to be spheres, one placed at each corner of the cubes. The cubes have an edge length of d at the end of the sintering process.

The radius of the pores, r decreases as the specimen sinters. Let us define a non-dimensional parameter

$$\alpha = \frac{r}{d}$$

Derive an equation that relates linear strain to α , and then make a plot of the linear strain as a function of α , where $0.35 < \alpha < 1$.

3. Surface Tension

Show that the free surface of a spherical pore, within a whole body, feels a normal traction pulling inwards towards the center of the pore, which is given by

$$\sigma_n = \frac{2\gamma_s}{r}, \text{ where } \gamma_s \text{ is the surface energy and } r \text{ is the radius of curvature of the pore.}$$

Confirm the units on both sides of the above equation.

4. The Chemical Potential

Write a short paragraph (about 100 words) on the origin of the gradient of the chemical potential, $(\frac{d\Delta\mu}{dx})$, in the sintering process, with reference to the equation for diffusional flux which is given by

$$j = \frac{D}{\Omega k_B T} \frac{d\Delta\mu}{dx}$$

In your narrative, please discuss, (i) the fundamental nature of the chemical potential, (ii) its relevance to the mechanism of sintering, and (iii) the significance of the chemical potential gradient.

5. Significance of Diffusion in Sintering

- (i) Give a short definition of "solid state" diffusion in the context of sintering.
- (ii) Explain with diagrams if you wish, how diffusion enables the "mechanism" of sintering that we have discussed in class at great length.
- (iii) Comment on the relative significance of volume and grain boundary diffusion.

6. Differential in the Rate of Diffusion of Cations and Anions in an Oxide.

Consider sintering of ZrO_2 from powders into a dense body by the mechanism that we have discussed in class.

Zirconia is an ionic ceramic where zirconium ions have a charge of +4, i.e. Zr^{4+} , while oxygen ions carry a charge of -2, which satisfies the charge neutrality condition in zirconia.

It so happens that zirconium and oxygen ions diffuse at different rates such that

$$D_{\text{Zr}^{4+}} \ll D_{\text{O}^{2-}}$$

•Give physical arguments why,

- (i) Why is it necessary to transport both Zr^{4+} and O^{2-} in the sintering process?
- (ii) Why is it necessary to transport two oxygen ions for every one zirconium ion?
- (iii) Can you give arguments that underpin the following description of the overall coefficient of diffusion

$$D_{\text{ZrO}_2} = \frac{\left(D_{\text{Zr}^{4+}}\right)\left(\frac{1}{2}D_{\text{O}^{2-}}\right)}{\left(D_{\text{Zr}^{4+}}\right) + \left(\frac{1}{2}D_{\text{O}^{2-}}\right)}$$

Hint: Consider limiting cases where

$$D_{\text{Zr}^{4+}} = D_{\text{O}^{2-}}$$

$$D_{\text{Zr}^{4+}} = 2D_{\text{O}^{2-}}$$

$$D_{\text{Zr}^{4+}} \ll D_{\text{O}^{2-}} \quad \text{case (x)}$$

$$D_{\text{Zr}^{4+}} \gg D_{\text{O}^{2-}}$$

In reality case (x) is true, that is the oxygen ions diffuse much faster than the zirconium ions. In this instance show that $D_{ZrO_2} \approx D_{Zr^{4+}}$

7. Units in the Eq. for Diffusional Flux

The equation for diffusional flux is given by:

$$j = \frac{D}{\Omega k_B T} \frac{d\Delta\mu}{dx} \quad (\text{Eq. 1})$$

Remember that we derived that $\Delta\mu = (\sigma_A - \sigma_B)\Omega$ where "A" refers to the grain boundary potential and "B" to the potential at the surface of the pore. We assumed that $\sigma_A \approx 0$ and the $\sigma_B = \frac{2\gamma_s\Omega}{r}$

(i) Derive the units for both sides of the equation and show then to be the same.

(ii) How will the units change if the Boltzmann's constant, k_B , is replaced by R , the gas constant. What is the difference between the units of these two quantities?

8. Volume and Grain Boundary Diffusion

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

$$t_s = \frac{1}{132} \frac{k_B T d^4}{(dD_{vol})\gamma_s\Omega} \quad \text{or} \quad = \frac{1}{132} \frac{k_B T d^3}{(D_{vol})\gamma_s\Omega}$$

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.

Please 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.

9. The Arrhenius Equation - the Activation Energy

(i) What is the physical significance of the activation energy, Q , in the equation for solid-state diffusion which is expressed in the Arrhenius form, as given just below?

$$D = D_0 e^{-\frac{Q}{RT}}$$

(i) Why is the activation energy for volume diffusion greater than for boundary diffusion?

(ii) If Q has a value of 500 kJ mol⁻¹, what is its value in eV?

(iii) What will be the units for Q if the above equation is written as $D = D_0 e^{-\frac{Q}{k_B T}}$, where k_B is the Boltzmann's constant.

10. Graphing the Arrhenius Equation

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

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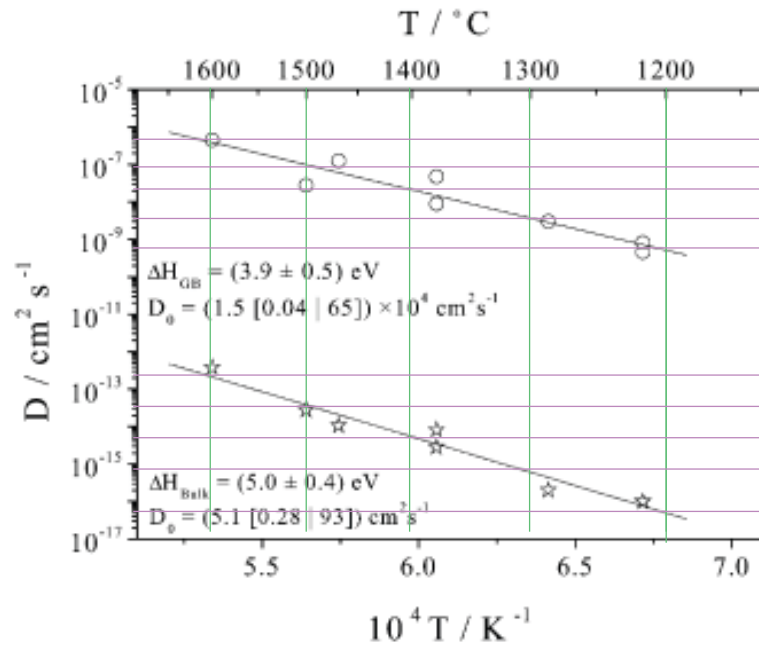


Fig. 3. Temperature dependency of ^{96}Zr tracer diffusivities. Symbols correspond to bulk diffusion ($\star$), and grain boundary diffusion ($\circ$), respectively.

The figure just above gives the data for the diffusion of the cation in zirconia (i.e. Zr^{4+}) for grain boundary (the upper plot) and volume diffusion (the lower plot). The activation energies are given as 3.9 eV and 5.0 eV respectively.

Derive the values for the activation energy by simple numerical analysis by hand and show whether or not your estimates agree with the values for the activation energies given above for grain boundary and volume diffusion.