06F: Problems Related to Diffusion

Homework Problems

Please refer to the following website for values for the diffusion coefficient, Omega etc. The website is organized into the properties of different classes of materials.. such as face centered cubic, metals, ceramics etc. It does not have an index but you can easily find the content of each chapter by clicking on it.

https://engineering.dartmouth.edu/defmech/

The problems explore different aspects of the diffusion coefficients. So each is given the appropriate heading.

The Pre-exponential

From Eq. (1) in the notes on Diffusion we had that

$$\Gamma = \upsilon_D e^{-\frac{Q}{RT}}$$

$$D_{gb} = \frac{1}{4}\Gamma a^2 = \frac{\upsilon_D a^2}{4} e^{-\frac{Q}{RT}} = D_{OB} e^{-\frac{Q_B}{RT}} \quad . \quad D_{OB} \text{ It has units of } \mathrm{m^2 s^{-1}}$$

Caveats: (i) Note that boundary diffusion is denoted either by the subscript "gb" or by "B" – they are the same. (ii) the above equation assumes two diffusion in two dimensions in the boundary; in volume diffusion the atom movements is three dimensional so that "4" will be replaced by "6". (iii) The value for the vibration frequency may be assumed to be the Debye Frequency (do not worry about what it is) which is $10^{13}\mathrm{s}^{-1}$.. however, this is a very significant approximation. The actual frequency can differ by one or two orders of magnitude.

The interatomic spacing a is given by $a = \Omega^{1/3}$ where Ω is the volume occupied by one atom species in the crystal (it is not the radius of the atom).

Omega is calculated from the molecular wt, the density and the Avogadro's Number,

$\Omega = \frac{M_W}{\rho N_A}$ (be very careful with the units).

In W the data for boundary diffusion is given not as D_B but as its product with the boundary width, δ or δ_B *or* δ_{gb} (since diffusion through the boundary always occurs across the boundary width). To a good approximation you can assume that

$\delta_B \approx 1.5\Omega^{1/3}$ which assumes that the width of the boundary is 1.5 times the spacing between the crystal planes within the crystal.

Now answer the following question:

Please go to Chapter 4 in the Website. It gives data for six metals with fcc structure.

(i) It gives data for $\delta_B D_{OB}$. Calculate D_{OB} using $\delta_B \approx 1.5\Omega^{1/3}$, for the six metals. How far do they agree with one another?

(ii) Now compare D_{OB} with D_{OV} the preexponential for volume diffusion. How far do they agree with each other?

Take away: diffusion coefficients can have considerable spread both in experimental measurements and theoretical estimates. Often they can be estimated only to within a factor or ten or one hundred. If you achieve consistent data within a factor of 2 then that is very good.

Normalization of the Diffusion Data with the melting Point

(i) Make Arrhenius plots for D_{OV} normalizing the temperature with the melting points (remember to use K) for three metals,

Ni, Cu and Pb. Comment on the degree of agreement shown in this plot.

(ii) Make Arrhenius plots for D_V and D_{OB} (after dividing the given data by the width of the boundary) on the same plot and comment on the difference between their magnitude and their temperature dependence.

Use copper as an example.

(iii) Now make another plot for dD_V where d is the grain size, and $\delta_B D_B$. Assume three values for the grain size, d, 2μm, 0.2 μm and 0.02μm. Comment on the relative shifts between these two plots when you change the grain size.