01G The Arrhenius Equation

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

(i) Separation of Variables

Note that in Eq. (1) only d and T are control variables.. the others are material parameters. Futhermore the influence of the particle size and temperature can be separated, that the influence of one can be measured by keeping the other variable constant.

What about $\delta_{gb} D_{gb}$?

Notes:

(ii) Significance of δ_{gb}:

This is the effective width of the boundary which serves as a channel for the diffusion of mass along the boundary. It can be assumed to be essentially equal to $\Omega^{\frac{1}{3}}$, that is the interatomic distance in the boundary. Therefore, like D_{gb}, it is a material parameter. Since it never possible to separate the coefficient of grain boundary diffusion from the cross-section of grain boundary diffusion, it is customary to write them together as

$\delta_{gb} D_{gb}$.

(iii) The temperature dependence of Eq. (1) is dominated by the diffusion coefficient since it depends exponentially on temperature. The contribution from the change in $k_B T$, when temperature changes, is negligible in comparison. For example a factor of two change in $k_B T$ can cause several orders of magnitude change in the coefficient of diffusion.

The general form of diffusion coefficients is as follows

$$D = D_O exp\left(-\frac{Q}{RT}\right) \qquad (2)$$

Here D_O is called the pre-exponential. Like D it has units of $m^2 s^{-1}$.

Q is the activation energy with units of kJ mol^{-1}, eV (1 eV = 96 kJ $mole^{-1}$; a number 100 is easy to remember and is a good approximation)

R is the gas constant equal to 8.31 J mol^{-1} K^{-1}

T is the temperature in Kelvin.

(iv) Plots of the Arrhenius Equation: Normalization with respect to the melting temperature.

Let us consider the general case of Eq. (2)

Taking natural log of both sides

$$\ln D = \ln D_O - \frac{Q}{R}.\frac{1}{T} \qquad (3)$$

For plotting with log to the base 10 (easier to interpret) we recognize that

$\ln_e x = 2.3\log_{10} x$, ($\ln_e x = \ln_e 10 * \log_{10} x$)

Therefore we have that

$$\log D = \log D_O - \frac{Q}{2.3R}.\frac{1}{T}$$ (we omit writing the base 10 and so on) (4)

Since Q is usually quoted in kJ mol^{-1}, and T is often above 1000 K (i.e. 923 °C), it is convenient to write Eq. (4) as

$$\log D = \log D_O - \frac{(Q/1000)}{2.3R}.\frac{1000}{T} \tag{5}$$

Often it is possible to normalize Eq. (5) with respect to the melting temperature T_M since the activation energy when divided by T_M is approximately a universal number.

(A physical explanation for the above statement is that both the activation energy, Q, and the melting temperature, T_M are related to the strength of the bonds among the atoms. This relationship is only approximate. It does not necessarily work all the time, still it is useful to know of it.)

With this normalization Eq. (5) becomes

$$\log D = \log D_O - \frac{Q}{2.3RT_M}.\frac{T_M}{T} \tag{6}$$

Let us see how well the normalization given by Eq. (6) can work. In the figure just below we consider five metals with very different melting points. For example,

Li T_M = 180 °C

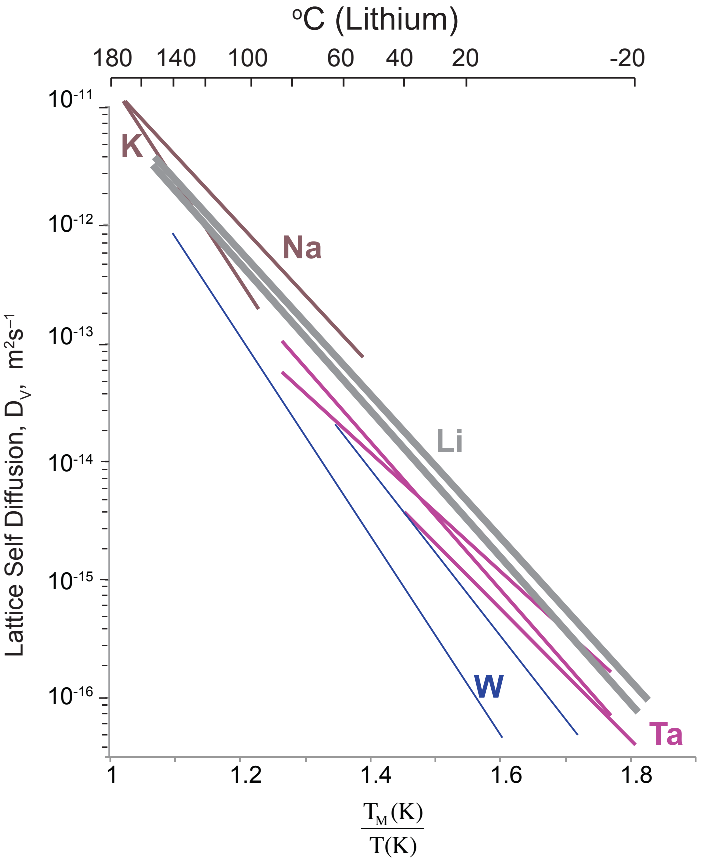
Na 98 °C

K 64 °C

Ta 3017 °C

W 3422 °C

Despite these wide differences in the melting temperature the diffusion coefficients are separated by about one order of magnitude when plotted in the normalized Arrhenius plots.



(v) Determination of Q from the Arrhenius plot.

As an example let us consider the Arrhenius plot for the lattice (volume) diffusion coefficient for the metal Li (that is, Li atoms diffusing within the lithium crystal).

We shall consider the example of Eq. (6) although the method is totally general.

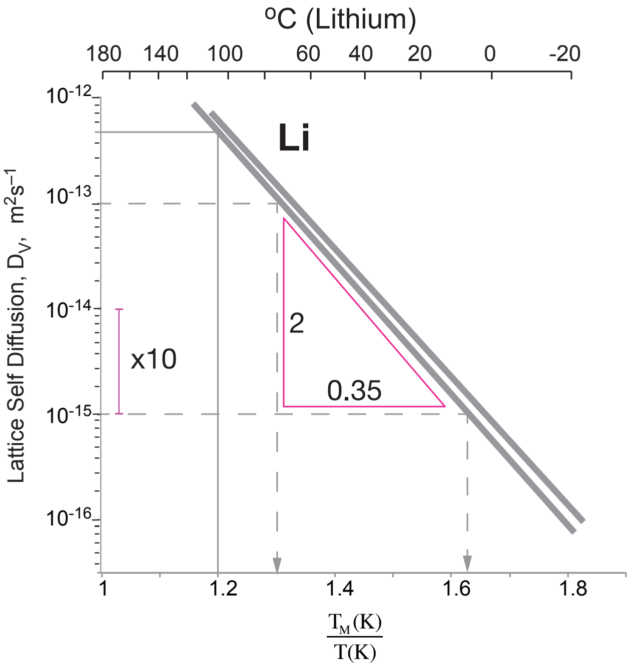
The plot of the data are shown on the next page.

Please make a note of the axes.

- The y-axis is plotted a $\log_{10}$(D) in m^{2}s^{-1}. We write the actual value rather than the log value, for example 10^{-14} is not written as -14 (that is the true logarithm of the number) but instead simply as 10^{-14}. The logarithmic nature of the plot is seen immediately by noting that every order of magnitude change in the number is separated by the same distance (in logarithm - a factor become a constant spacing in the scale).

- The x-axis usually has values near one since we are dealing with a fraction of the melting point. The higher temperature is to the left since we are plotting $\frac{1}{T}$.

- Please note that it is customary to give the temperature in °C along the x-axis on the top as shown in the figure.



- Let us calculate Q. Taking a derivative of Eq. (6) we obtain

$$\frac{\Delta \log D}{\Delta(\frac{T_M}{T})} = \frac{Q}{2.3RT_M}. \qquad (7)$$

From the graph we have that the left hand side in Eq. (7) is equal to 2/0.35, so that

$$Q = 2.3RT_M * \frac{2}{0.35}$$

$R = 8.31$ J $mol^{-1}K^{-1}$; $T_M = 180+273 = 453$ K

Therefore, Q = 59,305 J mol^{-1} = 59.3 kJ mol^{-1}

Notice also how rapidly the diffusion coefficient accelerates with temperature. For example increasing the temperature from about 10°C to 60°C increases the coefficient of diffusion by a factor of about 100.

Let us now consider diffusion in Zirconia

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

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

1594 *M.A. Taylor et al. / Journal of the Europea*

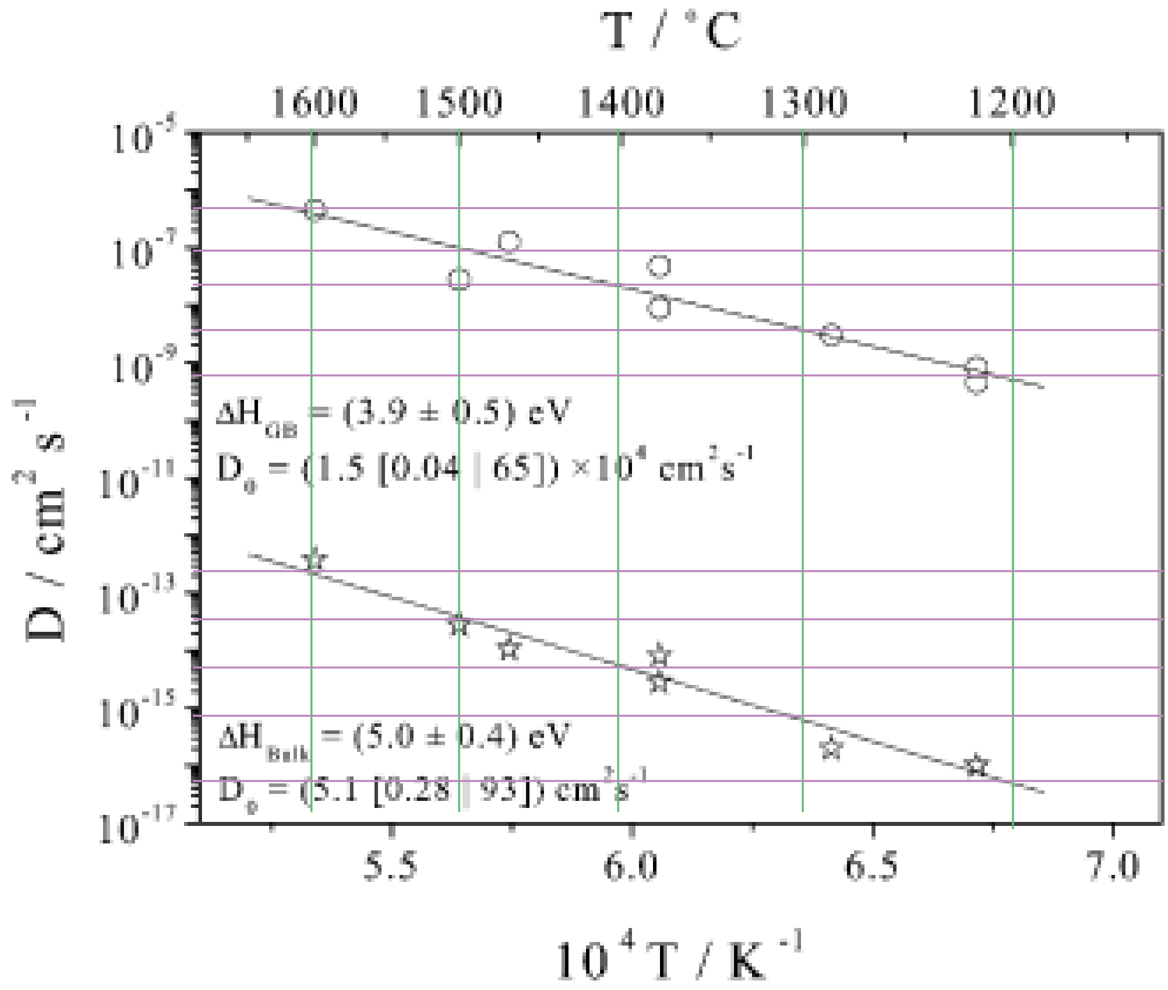


Fig. 3. Temperature dependency of ^{96}Zr tracer diffusivities. Symbols correspond to bulk diffusion (☆), and grain boundary diffusion (○), respectively.

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

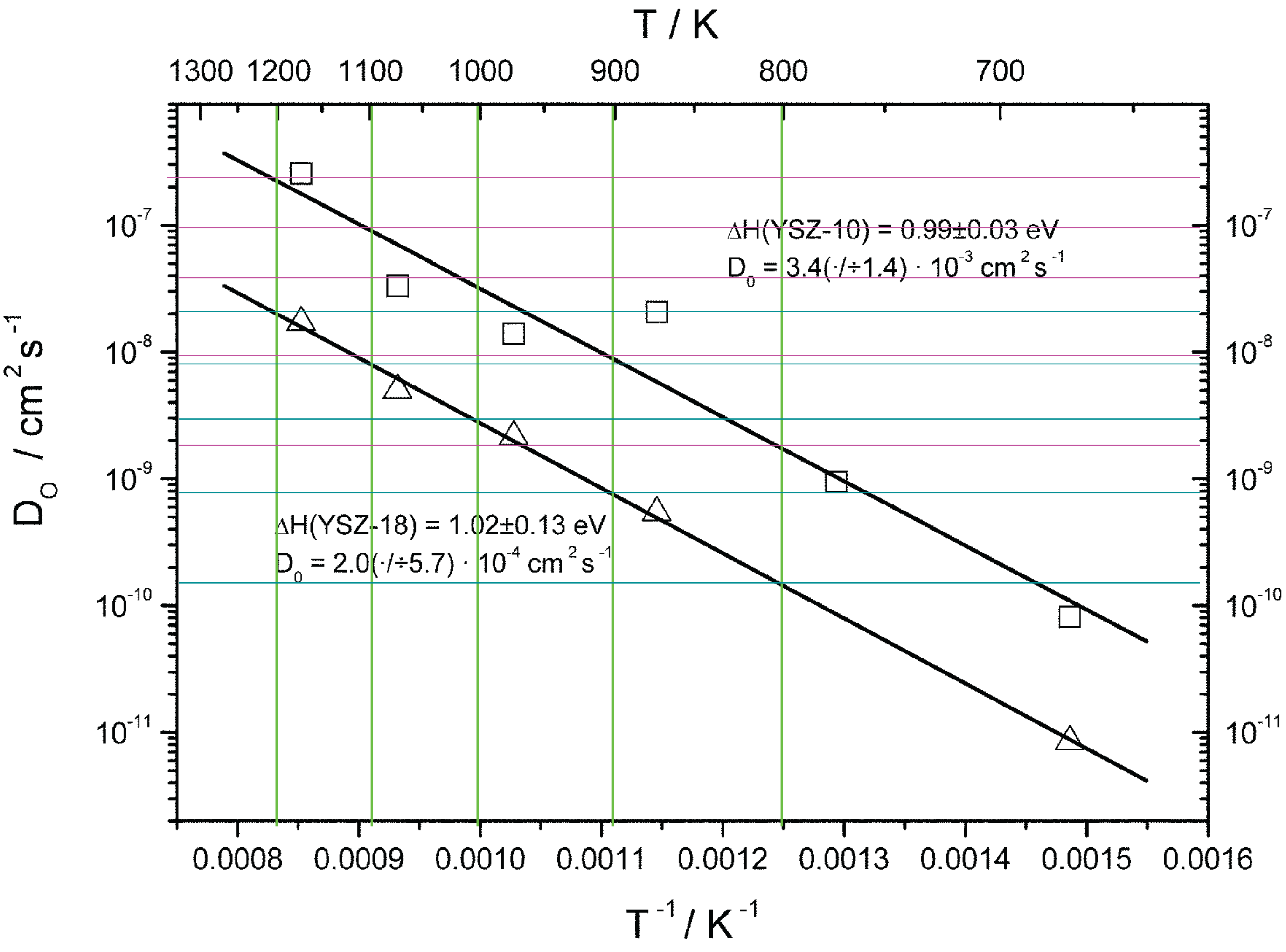


Fig. 2 Arrhenius plot of experimental oxygen diffusivities in YSZ-10 (squares) and YSZ-18 (triangles). The corresponding activation enthalpies and pre-exponential factors are included into the plot.

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.

(2) 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.