

23: Diffusion

What is Diffusion?

In all instances considered below diffusion coefficient or diffusivity has units of m^2s^{-1} .

Biology

"Differentiation of noncancerous tissue and cancer lesions by apparent diffusion coefficient values in transition and peripheral zones of the prostate"

<https://doi.org/10.1002/jmri.20251> value is $0.4 \times 10^{-3} \text{ mm}^2\text{s}^{-1}$, or $0.4 \times 10^{-9} \text{ m}^2\text{s}^{-1}$

Fluids and Viscous Glass

Stokes Einstein Equation: related viscosity to diffusion in liquids

$$\eta = \frac{k_B T}{6\pi\Omega^{1/3} D} \quad \sigma_s = \eta \dot{\epsilon}$$

Check units

viscosity units Pa s, $k_B T$ has units of J per unit of atom species (can be an atom or a molecule), RT where $R = k_B N_A$ units are $\text{J mol}^{-1} \text{K}^{-1}$, $R = 8.31 \text{ J mol}^{-1} \text{K}^{-1}$, THEREFORE RT has units of J mol^{-1} . $\Omega^{1/3}$ units m.

Right Hand Side: $\frac{\text{J} / \text{atom}}{\text{m} \cdot \text{m}^2 \text{s}^{-1}} = \frac{\text{Pa} \cdot \text{m}^3}{\text{m}^3 \text{s}^{-1}} = \text{Pa s}$ as for viscosity.

Thermal Diffusivity

"EARTH TEMPERATURE AND THERMAL DIFFUSIVITY AT SELECTED STATIONS IN THE UNITED STATES"

Kusuda T, Achenbach PR. Earth temperature and thermal diffusivity at selected stations in the United States. National Bureau of Standards Gaithersburg MD; 1965 May 1.

Salazar A. On thermal diffusivity. European journal of physics. 2003 May 13;24(4):351.

$$k_{\text{thermal diffusivity}} = \frac{K}{\rho C_p}$$

Here K is the thermal conductivity, ρ is the density and C_p is the specific heat at constant pressure.

Check Units: K has units of $\text{W m}^{-1} \text{K}^{-1}$ or $\text{J s}^{-1} \text{m}^{-1} \text{K}^{-1}$, ρ is kg m^{-3} , C_p is $\text{J K}^{-1} \text{kg}^{-1} \text{g}^{-1}$ so the RHS is $\frac{\text{J}}{\text{s m K}} \frac{\text{m}^3 \text{K kg}}{\text{J}} = \frac{\text{m}^2}{\text{s}}$

consistent with the units of diffusion coefficient.

In Glass

"Exchange and Diffusion of ion in Glass"

It is a mechanism for strengthening glass by inducing a compressive stress near the surface of glass which increases its fracture strength (Gorilla Glass). Start with a glass which has sodium in it. immerse is in molten salt of potassium, and by diffusion K diffuses and Na diffuses out. The K atoms are larger than Na atoms; therefore ion exchange processs induces a compressive stress.

Need to control the depth of ion exchange. Typically the depth should be about ten times the flaw - $50 \mu\text{m}$ or so.

Use the following equation that relates the diffusion distance to the diffusion coefficient (which is a function of temperature) and time.

$$6Dt = L^2$$

The diffusion coefficient times the time equals the square of the diffusion distance

Check Units $m^2s^{-1} \times s = m^2$

In Semiconductors

Doping silicon to shallow depths to create "n" and "p" type semiconductors

$$6Dt = L^2$$

"Diffusion in Silicon" S. W. Jones; Jones SW.
 Diffusion in silicon. IC Knowledge LLC. 2008
 Apr 25:23-61.

Diffusivity of P in Si

$$D_{P/Si} = 44.2 \exp\left(-\frac{437 \text{ kJ/mol}}{RT}\right) \text{ cm}^2\text{s}^{-1}$$

Boron in Silicon

$$D_{B/Si} = 0.76 \exp\left(-\frac{346 \text{ kJ/mol}}{RT}\right) \text{ cm}^2\text{s}^{-1}$$

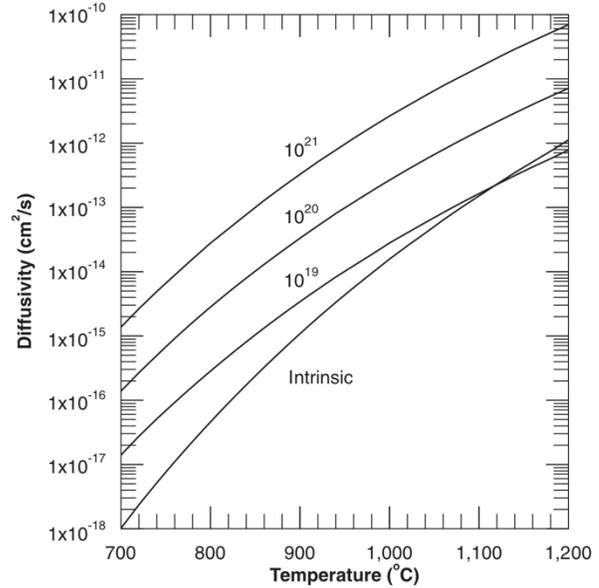


Figure 1.15: Diffusivity of boron in silicon versus temperature and boron concentration. Calculated from equations 1.72 through 1.75.

In Crystals

Self Diffusion in Pure Metals

Norman Peterson: [https://doi.org/10.1016/0022-3115\(78\)90234-9](https://doi.org/10.1016/0022-3115(78)90234-9)

$$6Dt = L^2$$

Diffusion can lead to time dependent deformation

Diffusion is the basis of making dense ceramics from powders by a process known as sintering

Diffusion is the basis of precipitation and dispersion strengthening

"Self-Diffusion and Impurity Diffusion in Pure Metals: Handbook of Experimental Data", Neumann and Tuijin, Elsevier 2009

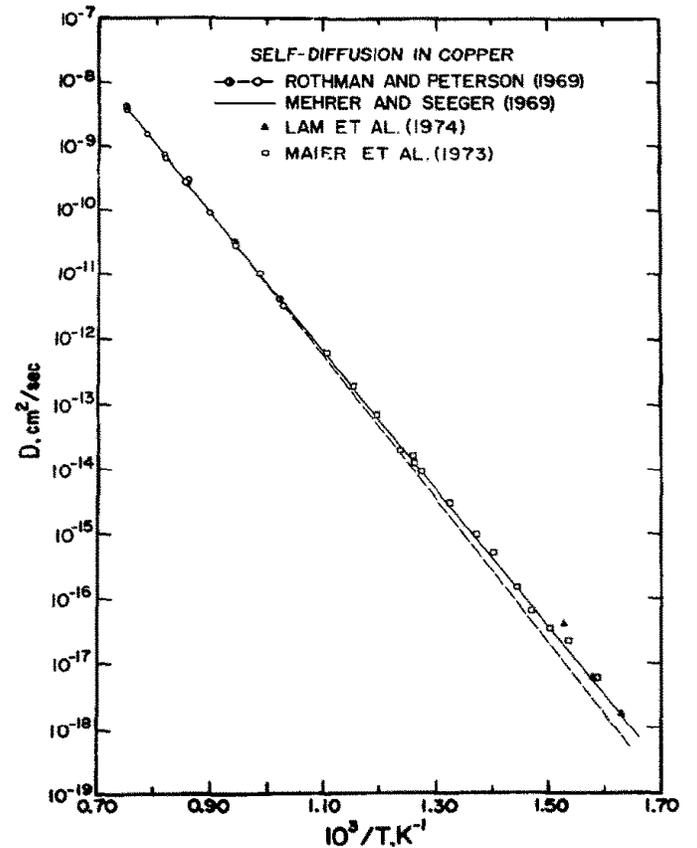
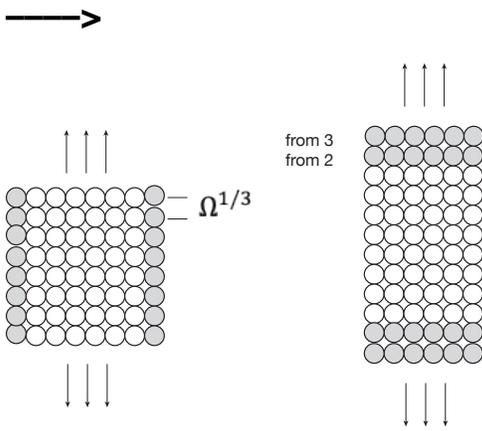


Fig. 7. Log D vs. reciprocal absolute temperature for tracer self-diffusion in copper that shows the data of \circ : Rothman and Peterson [61], \blacktriangle : Lam et al. [80], \square : Maier et al. [81]. The solid line is from the analysis by Mehrer and Seeger [59] of the results of Rothman and Peterson [61]. The dashed

Flow Chart

•Describe the geometrical relationship between the movement of atoms and strain



•Consider the rate of movement of atoms by diffusion



•Describe the equations that prescribe the influence of applied stress to the diffusion flux



•Obtain the equation for the strain rate in terms of the applied stress, the grain size and the temperature.

$$\dot{\epsilon} = A \frac{\sigma^n}{d^p} D_0 e^{-\frac{Q}{RT}}$$

Diffusion units of m^2s^{-1} and has the form

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

Need to understand this form of the diffusion coefficient.

Significance of the Arrhenius for of the Diffusion Coefficient

Units:

Overall units: $m^2 s^{-1}$. These units lead to a very significant equation that links diffusion to an effective diffusion distance, L , in time t ,

$$6Dt = L^2 \tag{1}$$

The factor of six arises because diffusion can potential occur in six directions, $\pm x, \pm y, \pm z$.

Diffusion coefficients are handbook values, with one caveat, they apply to the diffusion of a specific species in the host of a the same or a different species. The two examples are:

- self diffusion where the diffusing and the host species are the same - this is relevant to deformation induced by diffusion.
- diffusion of a foreign species in a host - and example is the diffusion of the dopant Al in Si to create an "n" type layer, a precursor to the creation of a p-n junction diode.
- Q/RT is non dimensional as it must be since an exponential of x can be expanded into a power series of x .
- RT has units of $JK^{-1}mol^{-1}$, and T is in degrees K, therefore RT has units of $J mol^{-1}$.
- It follows that Q also has units of $J mol^{-1}$. Typical values range from $50 kJ mol^{-1}$ to $300 kJ^{-1}$. It is related to the enthalpy of formation therefore it generally scales with the melting temperature (in K), so that

$\frac{Q}{RT_M} \approx$ a universal quantity for a given class of crystals ; this means that the diffusion coefficients for different metals

when grouped in classes such as fcc, bcc structures and so on, can be normalized in the following way

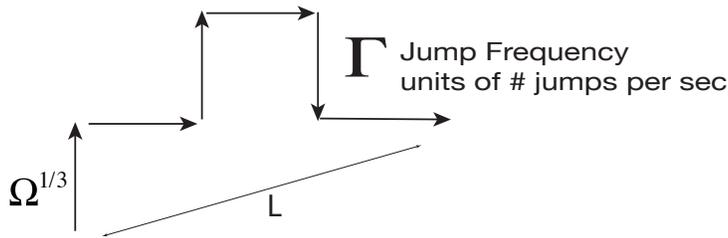
$$D = D_0 e^{-\frac{Q}{RT} - \frac{T_M}{T}} \quad (2)$$

That is if the diffusion coefficients for different metals in the same group are plotted against $\frac{T_M}{T}$ they fall more or less on a master curve.

Equations (1) and (2) are the most significant aspects of the phenomenological significance of the coefficient of self-diffusion.

Mechanism of (self) Diffusion

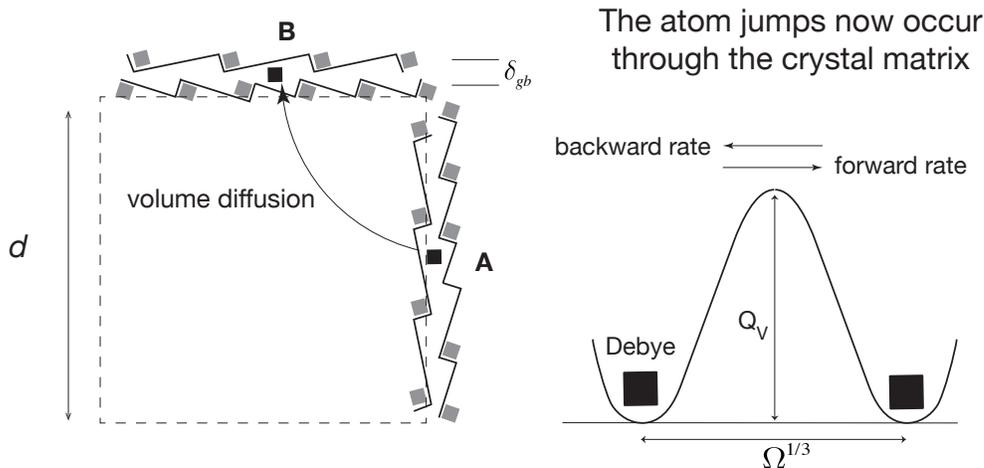
The mechanism of diffusion in crystals (or solids) is discreet atom jumps, on at a time that leads to diffusion overall. In this two parameters are to be considered as in the schematic below



$$\text{Diffusion coefficient} = \frac{\text{\#of jumps per second}}{6} (\text{jump distance})^2 = \frac{1}{6} \Gamma \Omega^{2/3}$$

The factor of six because the atom can jump in six possible directions in a crystal. Note that above is consistent with the units of the diffusion coefficient.

The next question we ask is what determines the jump frequency?



The jump requires going "over an energy hill", which we call the activation energy.

Concept is that the atom vibrating (oscillating) in its native site at a certain frequency (called the Debye Frequency which has a value of $\sim 10^{13} \text{s}^{-1}$), and now then it jump over the activation barrier.

The jump frequency = Debye Frequency x probability that the atom will succeed in making the jump. This probability is

$$D = \frac{1}{6} v_D (10^{13} \text{ s}^{-1}) \Omega^{2/3} \exp\left(-\frac{Q}{RT}\right)$$

given by $\exp\left(-\frac{Q}{RT}\right)$, Therefore,

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$