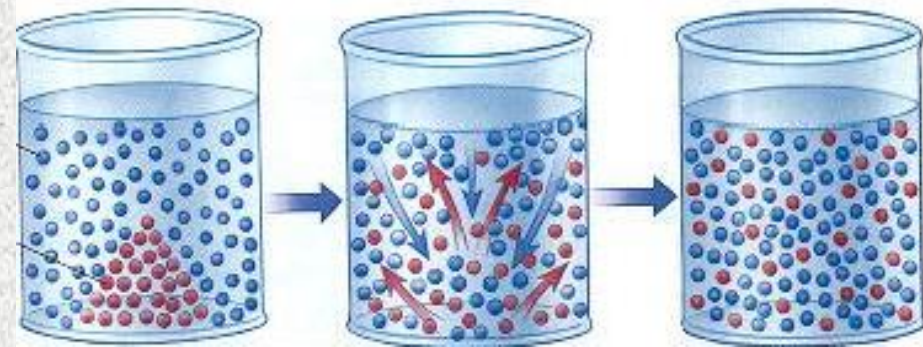
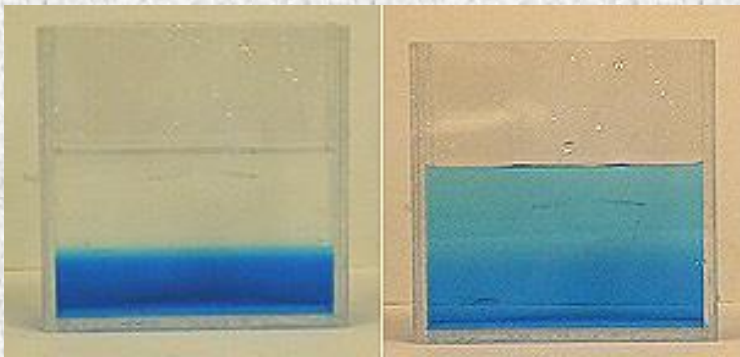


5-Diffusion: Atom Movement in Materials

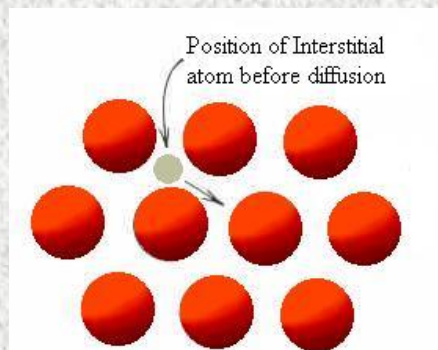
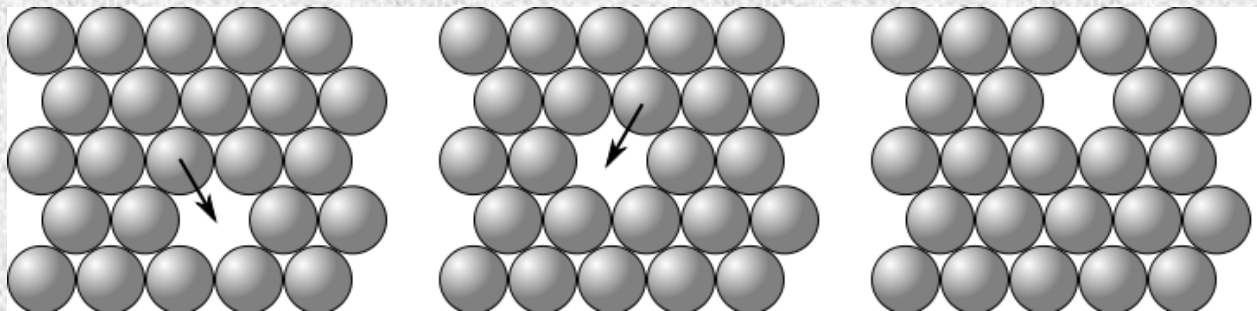


Primer in Materials Science
Spring 2021

Diffusion mechanisms

There are two important mechanisms by which atoms diffuse:

1. **Vacancy diffusion**: in self-diffusion and substitutional diffusion, an atom leaves its lattice site to fill a nearby vacancy. As diffusion continuous we get counter-current flow of vacancies
2. **Interstitial diffusion**: Small interstitial atom which present in the crystal moves from one interstitial site to another. No vacancy is required for this mechanism. This mechanism is more rapid than vacancy diffusion



Fick's First Law

rate of diffusion

General expression: flux of the i^{th} atom.

$$J_i = -A_i C_i \frac{\partial \mu_i}{\partial C_i} \frac{\partial C_i}{\partial x}$$

C – concentration of the i^{th} atom

μ - the chemical potential of the i^{th} atom

A – constant. The *atomic mobility* of the i^{th} atom

J – the flux of the i^{th} atom. [$\text{m}^{-2} \cdot \text{s}^{-1}$] number of atoms per second per meter square

$$D_i = A_i C_i \frac{\partial \mu_i}{\partial C_i}$$

$$J_i = -D_i \frac{\partial C_i}{\partial x}$$

D – Diffusion coefficient of the i^{th} atom

Example 5.1

A 5mm layer of MgO is deposited between layers of Ni and Ta to provide a diffusion barrier that prevents reaction between the two metals. At 1400°C Ni diffuse through the MgO ceramics to the Ta. Determine the flux of Ni that pass through the MgO. $D=9 \cdot 10^{-16}$ [m²/s] (Ni in MgO). $a_{Ni}=0.36$ nm (at 1400°C)

First lets find the Ni concentration at the boundary of the MgO. The concentration is 100% of Ni therefore is equal to Ni atomic density:

$$C1 := \frac{4}{a0^3} \quad C1 = 8.573 \times 10^{28} \frac{1}{m^3}$$

The concentration of Ni at the Ta/MgO surface is zero. so $C2=0$

$$D := 9 \cdot 10^{-16} \frac{m^2}{s} \quad \Delta x := 5mm$$
$$J := -D \cdot \frac{C2 - C1}{\Delta x} \quad J = 1.543 \times 10^{16} \frac{1}{s \cdot m^2}$$

$$Area := 20(mm)^2 \quad \text{Number_of_atoms_per_second} := J \cdot Area$$

$$\text{Number_of_atoms_per_second} = 3.086 \times 10^{11} \frac{1}{s}$$

Diffusion coefficient

The Diffusion coefficient is related to the Temp. by an Arrhenius equation:

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

D - diffusion coefficient [cm²/s]

- When the temperature is high the thermal energy permits the atoms to overcome the potential barrier and more easily move to new lattice site
- At high temperature the diffusion coefficient increases causing to larger flux of atoms.
- At low temperature (about 0.4 of T_m) the diffusion not significant

Example 5.2

The diffusion coefficient for Cr in Cr_2O_3 is $6 \cdot 10^{-19} \text{ [m}^2/\text{s]}$ at 727°C and is $1 \cdot 10^{-13} \text{ [m}^2/\text{s]}$ at 1400°C . Calculate:

- The activation energy
- The constant D_0

$$D1 := 6 \cdot 10^{-19} \frac{\text{m}}{\text{s}} \quad D2 := 1 \cdot 10^{-13} \frac{\text{m}}{\text{s}}$$

$$T1 := 1000\text{K} \quad T2 := 1673\text{K}$$

$$D1 := D0 \cdot e^{\frac{-E}{\text{Kb} \cdot 1000}} \quad D2 := D0 \cdot e^{\frac{-E}{\text{Kb} \cdot 1673}}$$

$$\frac{D1}{D2} = \frac{-E}{\text{Kb}} \cdot \left(\frac{1}{1000\text{K}} - \frac{1}{1673\text{K}} \right)$$

$$E := \ln\left(\frac{D1}{D2}\right) \frac{(-\text{Kb})}{\left(\frac{1}{1000\text{K}} - \frac{1}{1673\text{K}}\right)} \quad \frac{E}{\text{Av}} = 2.484 \times 10^5 \frac{\text{J}}{\text{mol}}$$

$$D0 := \frac{D1}{\frac{-E}{\text{Kb} \cdot 1000\text{K}}} \quad D0 = 5.742 \times 10^{-6} \frac{\text{m}^2}{\text{s}}$$

Diffusion Length

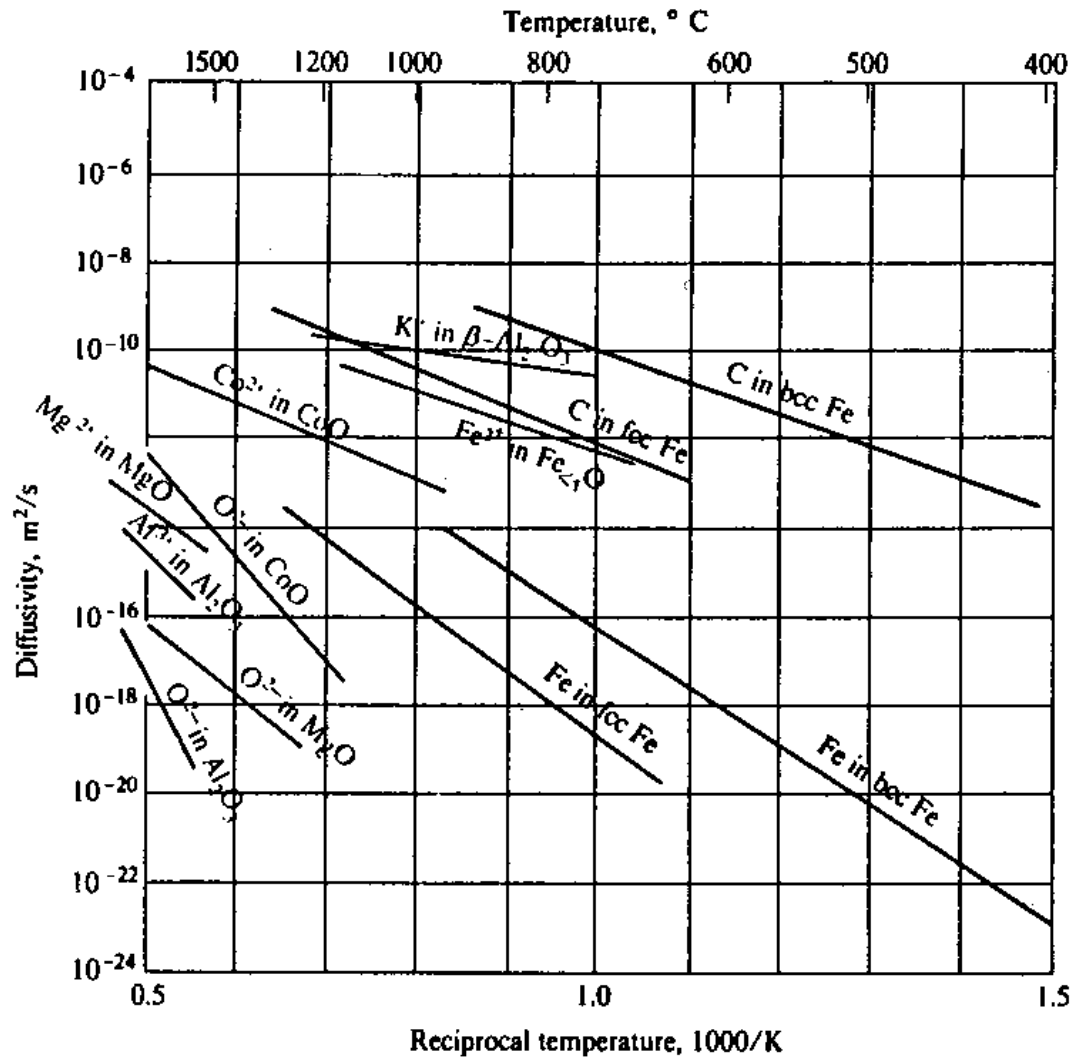
The Diffusion Length is the penetration distance of the diffused atoms

$$d = \sqrt{\beta \cdot D \cdot t}$$

t is the diffusion time

- $\beta=2$ in 1-dimension diffusion; $\beta=4$ in 2-dimensions diffusion; $\beta=6$ in 3-dimensions diffusion.
- For a rough estimation of the Diffusion Length people usually take $\beta=1$.

Diffusion Graphs



How to read the graph

- The graph shows some diffusion coefficient of several atoms in ceramics compounds as a function of Temperature.
- Diffusivity = diffusion coefficient.
- For example the diffusion coefficient of C in bcc Fe is 10^{-10} [m²/s] at about 750°C (Top scale) or at $1000/K=1$ (Bottom scale) which means at 1000K

Example 5.3

What is the diffusion coefficient of Co^{2+} in CoO at about 1420K? What is the diffusion coefficient of O^{2-} in CoO at the same temperature? Why is there such a large difference?

- 1420K corresponds to 0.7 in the bottom scale.
From that we can take the data to be:
- $D(\text{Co}^{2+}) @ 1420\text{K} \approx 10^{-12} \text{ [m}^2/\text{s]}$
- $D(\text{O}^{2-}) @ 1420\text{K} \approx 10^{-17} \text{ [m}^2/\text{s]}$

Both ions have the same valance so the difference comes from their ionic radii:

$r(\text{Co}^{2+}) = 0.0745 \text{ nm}$, $r(\text{O}^{2-}) = 0.140 \text{ nm}$.

The smallest the atom the higher the diffusion coefficient

Example 5.4

Please estimate the activation energy of diffusion coefficient of silver in pure copper from the figure attached. Could you please think why the activation energy of many metallic impurities in Cu are quite similar above 700 °C?

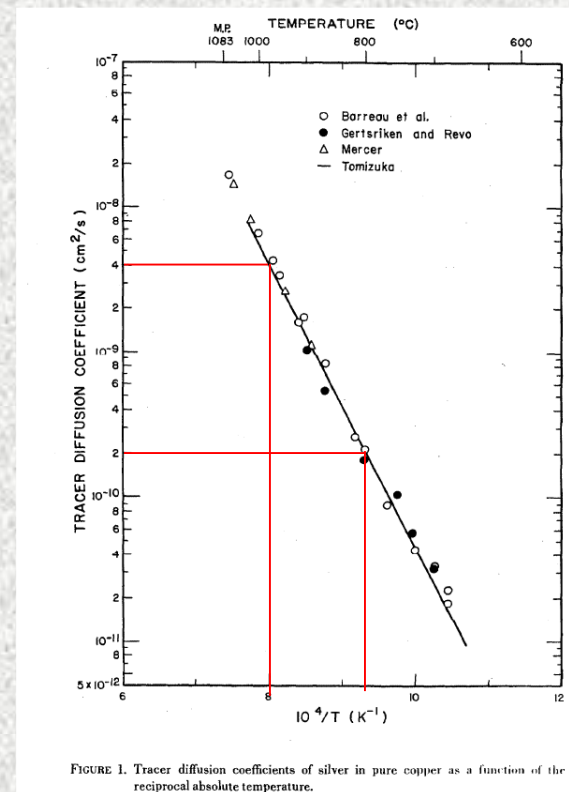


FIGURE 1. Tracer diffusion coefficients of silver in pure copper as a function of the reciprocal absolute temperature.

$$a) \ln D = \ln D_0 - E/K_b T$$

From the graph:

$$\ln(4 \times 10^{-9}) - \ln(2 \times 10^{-10}) = (-E/K_b)(8 \times 10^{-4} - 9.2 \times 10^{-4})$$

$$E = (2.996 / 1.2 \times 10^{-4}) \times 8.62 \times 10^{-5} = 2.15 \text{ [eV/atom]}$$

b) Since at this temperature the diffusion is through vacancies and the activation energy is for vacancy formation.

Example 5.5

Diffusion of most impurities in d3 metals subgroup, Ta, V and Nb is extremely slow, even so high temperature as 1500°C . a) Could you offer a short but reasonable explanation to this phenomenon? b) Diffusion of hydrogen in Nb-Ta alloys (METALLURGICAL TRANSACTIONS A, V13, 1675, 1982) is extremely fast even at 100°C . Could you explain such discrepancy?

- a) Even at 1500°C there is very small vacancy concentration and the lattice is very stiff.
- b) The hydrogen atoms diffuse in the small interstitial sites.

Example 5.6

Diffusion of Ag in Sn is rapid (at 200°C) but diffusion of Sn in Ag is orders of magnitude slower. Why? What direction will crystal planes move towards Sn or towards Ag?

- a) Since the melting point of Sn is 231.93°C , at 200°C the vacancy concentration is very large. In contrast, since the melting point of Ag is 961.78°C , at 200°C the vacancy concentration is much smaller.
- b) The panes move towards Ag.

Example 5.7

The Diffusion coefficient of sodium in graphite quickly drops when graphite is close to be saturate by sodium.
Can you suggest a reason?

The sodium atoms fill all the interstitial sites, so they can not move.