EMA5001 Lecture 2
Interstitial Diffusion & Fick's 1st Law

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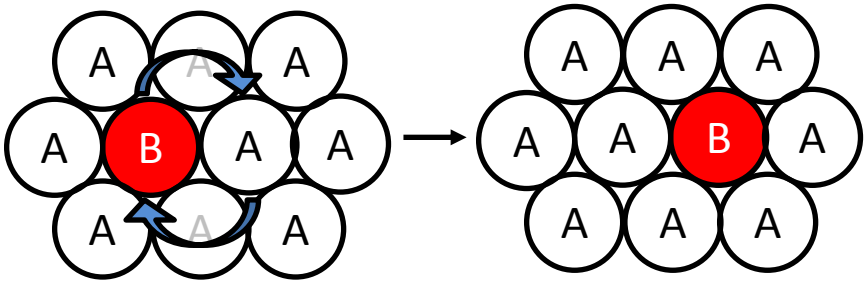
Substitutional Diffusion

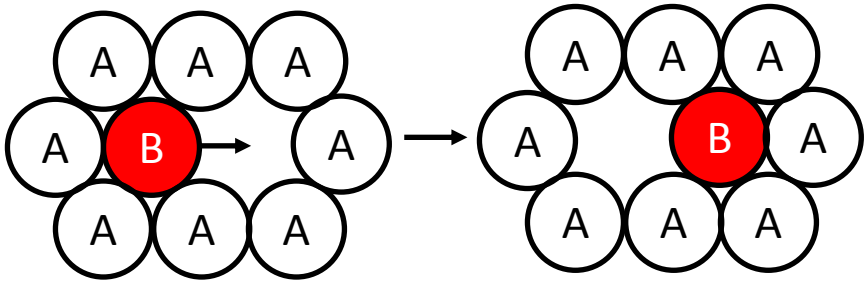
❑Different possibilities

Exchange Mechanism



May occur on surface
Higher activation energy

Vacancy Mechanism



Far more common in solids
Lower activation energy

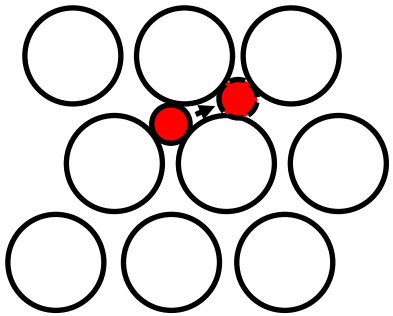
❑Features of substitutional diffusion via vacancy mechanism

- Size of diffusing atoms/ions: similar to surrounding matrix atom/ion size
- Successful jumping rate determined by
  - Frequency of jump attempts (thermal activation), &
  - Availability of vacancy (concentration)

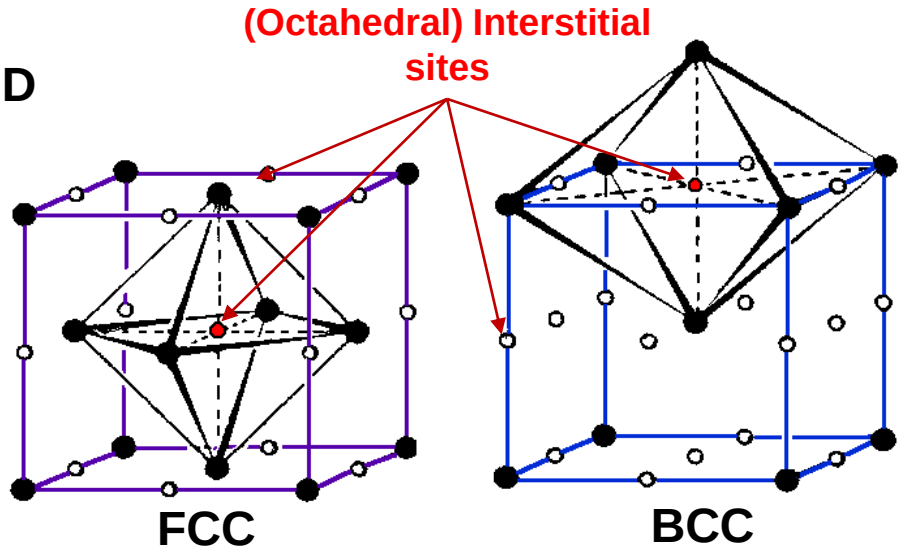
Interstitial Diffusion

❑Atoms/ions at interstitial sites

2-D



3-D



http://www.tf.uni-kiel.de/matwis/amat/def_en/kap_1/illustr/t1_3_3.html

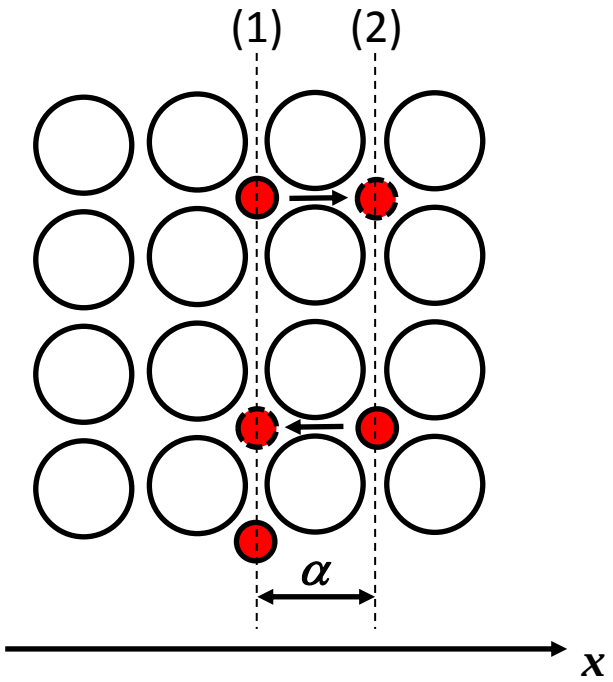
❑Features

- Size of diffusing atoms/ions - Much smaller than surrounding (matrix) atoms/ions
  - C diffusing through Fe: r_C ~ 70 pm vs. r_{Fe} ~ 140 pm
  - Cu diffusing through Si: r_{Cu+} = ~77 pm vs. r_{Si} ~ 110 pm
    http://en.wikipedia.org/wiki/Atomic_radius; http://en.wikipedia.org/wiki/Ionic_radius
- Successful jumping rate for dilute solid solution - Determined by thermal activation alone as neighboring interstitials typically are *rarely* occupied

Interstitial Diffusion as a Random Jump Process (1)

❑ Dilute interstitial solid solution of B in A

- Γ_B - average successful jump frequency (in unit of sec^{-1}) of interstitial atom B
- n_1 – area (number) density of B in plane (1)
- n_2 – area (number) density of B in plane (2)



In unit time, flux of B, J_B

from plane (1) to (2) $\overrightarrow{J_B} = \frac{1}{6}\Gamma_B n_1$

from plane (2) to (1) $\overleftarrow{J_B} = \frac{1}{6}\Gamma_B n_2$

Net flux of B along x direction: $J_B = \overrightarrow{J_B} - \overleftarrow{J_B} = \frac{1}{6}\Gamma_B (n_1 - n_2)$ in unit of $m^{-2}sec^{-1}$

Introduce α as jump distance of plane (1) from (2). For **simple cubic lattice**, volume concentration (in unit of m^{-3}) C_B at position (1) and (2) will be $C_B(1) = \frac{n_1}{\alpha}$ $C_B(2) = \frac{n_2}{\alpha}$

Interstitial Diffusion as a Random Jump Process (2)

❑ **Continue from p4**

$$J_{\mathbf{B}} = \frac{1}{6}\Gamma_B \alpha \left[C_B(1) - C_B(2)\right]$$

Since both lattice constant α and $C_B(1) - C_B(2)$ are very small,

$$\frac{C_B(2) - C_B(1)}{\alpha} = \frac{\partial C_B}{\partial x}$$

Then $$J_{\mathbf{B}} = \frac{1}{6}\Gamma_B \alpha \left[C_B(1) - C_B(2)\right] = -\frac{1}{6}\Gamma_B \alpha^2 \frac{C_B(2) - C_B(1)}{\alpha} = -\frac{1}{6}\Gamma_B \alpha^2 \frac{\partial C_B}{\partial x}$$

$$J_B = -\frac{1}{6}\Gamma_B \alpha^2 \frac{\partial C_B}{\partial x}$$

Define **diffusion coefficient** $D_B = \frac{1}{6}\Gamma_B \alpha^2$ $\boldsymbol{D_B}$ in unit of m^2/sec

We have

$$J_B = -D_B \frac{\partial C_B}{\partial x}$$

Fick's 1st Law

Other Considerations

- **Diffusion**

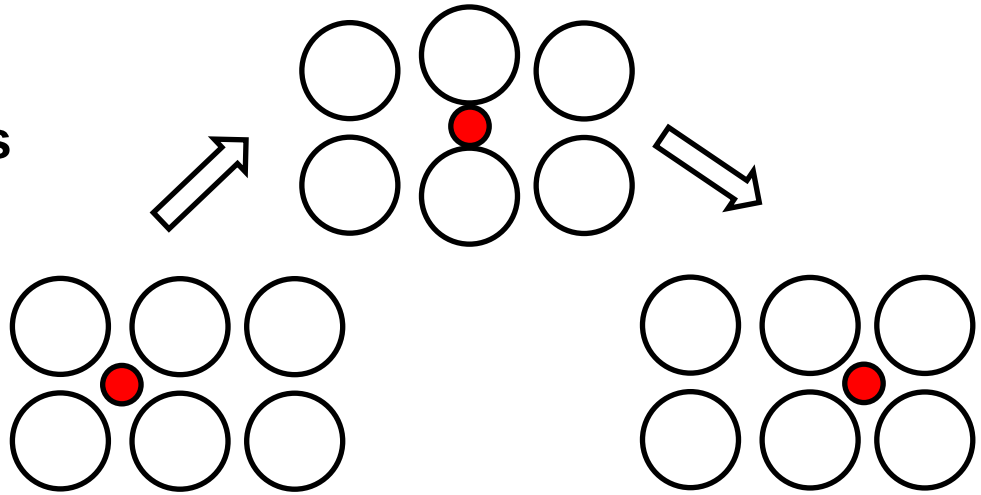
$$J_B = -D_B \frac{\partial C_B}{\partial x} \qquad D_B = \frac{1}{6}\Gamma_B \alpha^2$$

- **Impacts of lattice structures**
  - Other cubic lattice (e.g., FCC, BCC) - still applicable (need some derivation)
  - Non-cubic - D_B different along different crystal directions
- **Impacts of solute concentration**
  - Assumption: D_B constant for small difference in concentration
  - Over large concentration range: D_B different for different solute concentration
    - D_C in γ-Fe at 1000 °C is 2.5×10^{-11} m²/s at 0.15wt% carbon and 7.7×10^{-11} m²/s at 1.4wt%
- **Estimation of interstitial atoms jump frequency**
  - γ-Fe, FCC structure, lattice constant 0.37 nm, jump distance $\alpha = a/\sqrt{2} = 0.26$ nm At 1000 °C, $D_B = 2.5\times10^{-11}$ m²/s. Answer: 1) What is estimated successful jump frequency? 2) One in how many attempts succeeds with a jump?
    - Successful jump frequency: $\Gamma_C = 2.2 \times 10^9$ /s
    - Lattice vibration frequency: $\nu_C = 1.38\times10^{-23}$ J/K • (1000+273) K /(6.63×10^{-34} J s) = 2.6×10^{13} /s (from $kT = h\nu$) → **$\Gamma_C/\nu_C = 10^{-4}$**, one in 10,000 jump successful

Thermal Activation of Interstitial Diffusion (1)

- **Activation energy**
  - Migration energy barrier G_m
- **Proportion of high energy atoms**
  - Portion of atoms with energy higher than mean/equilibrium energy by G_m (m for migration)

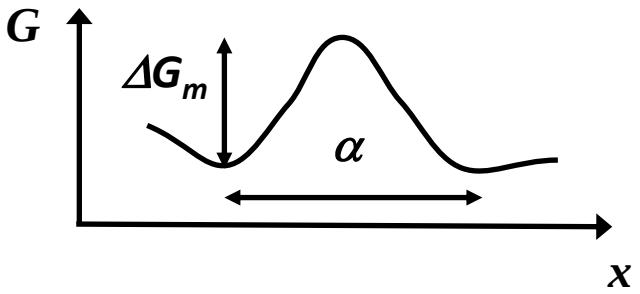
$$\exp\left(-\frac{\Delta G_m}{RT}\right)$$



- **Jump frequency**
  - ν - Thermal vibration frequency

(successful) jump frequency will be

$$\Gamma_B = \nu \exp\left(-\frac{\Delta G_m}{RT}\right)$$



Thermal Activation of Interstitial Diffusion (2)

- **Jump frequency** $\Gamma_B = \nu \exp\left(-\frac{\Delta G_m}{RT}\right)$

- **Diffusion coefficient** $D_B = \frac{1}{6}\Gamma_B \alpha^2$

Therefore, $D_B = \frac{1}{6}\alpha^2 \nu \exp\left(-\frac{\Delta H_m - T\Delta S_m}{RT}\right)$

$$D_B = \left[\frac{1}{6}\alpha^2 \nu \exp\left(\frac{\Delta S_m}{R}\right)\right]\exp\left(-\frac{\Delta H_m}{RT}\right)$$

Define

Frequency factor $D_{B0} = \frac{1}{6}\alpha^2 \nu \exp\left(\frac{\Delta S_m}{R}\right)$

Interstitial diffusion activation energy $Q_{ID} = \Delta H_m$

We have $\boxed{D_B = D_{B0} \exp\left(-\frac{Q_{ID}}{RT}\right)}$

Diffusion coefficient increases "exponentially" with T!

Thermal Activation of Interstitial Diffusion (3)

❑Some data

In BCC α-Fe

Interstitial atom	D_0 (mm²/s)	Q (kJ/mol)
C	2	84.1
N	0.3	76.1
H	0.1	13.4

Porter et al. Phase Transformations in Metals & Alloys, 3rd Ed (2009), CRC Press, p. 73

❑Obtaining Q and D_0 from measured D

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

We have

$$\ln D = \ln D_0 - \left(\frac{Q}{R}\right)\cdot\frac{1}{T}$$

Or

$$\lg D = \lg D_0 - \left(\frac{Q}{2.3R}\right)\cdot\frac{1}{T}$$