Chapter 5: Diffusion (1)

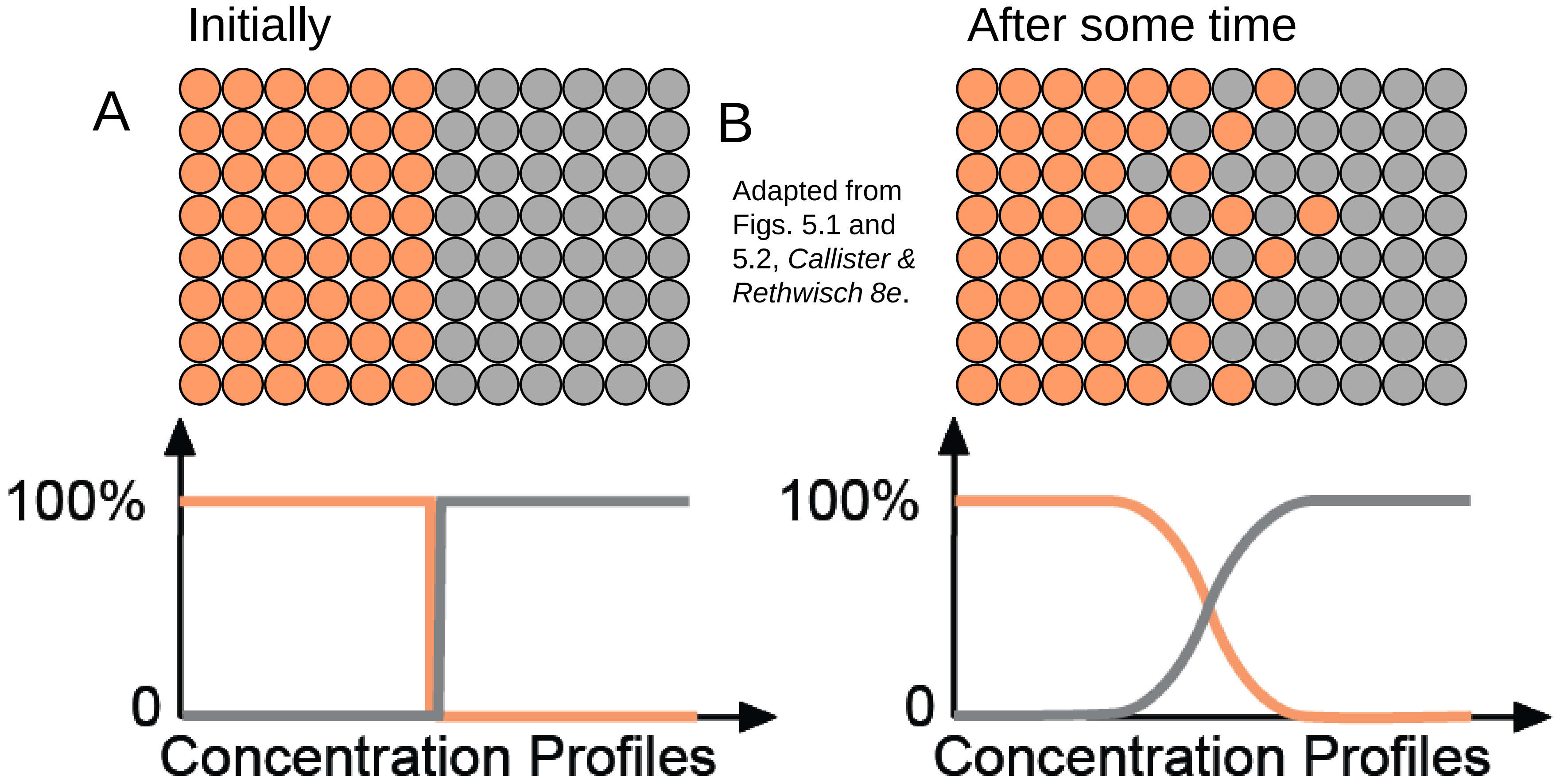
Diffusion - Mass transport by **random**, atomic (or molecular-scale) motion

ISSUES TO ADDRESS...

- How does diffusion occur?
- Why is it an important part of processing?
- How can the rate of diffusion be predicted for some simple cases?
- How does diffusion depend on structure and temperature?

Diffusion

- Interdiffusion: when joining **different** metals (or in other materials system), atoms (or other species) tend to migrate from regions of high conc. to regions of low conc.

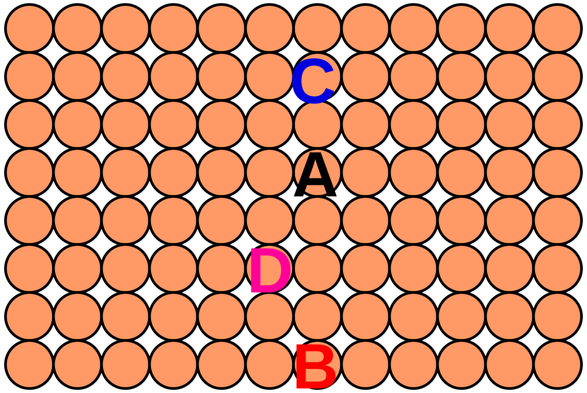


Adapted from Figs. 5.1 and 5.2, *Callister & Rethwisch 8e*.

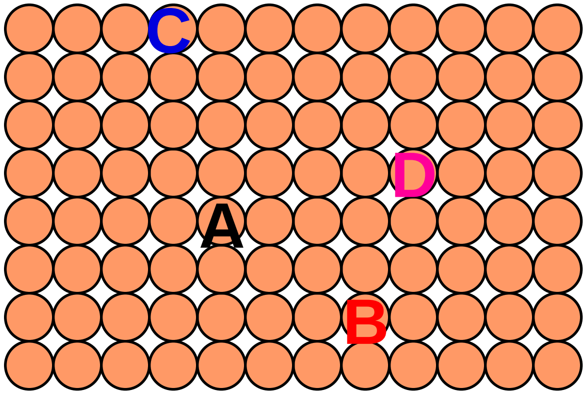
Diffusion

- Self-diffusion: Even in an pure elemental solid, atoms also migrate randomly via self-diffusion process.

Label some atoms



After some time



Examples of (Inhibiting) Diffusion

- **Different packaging for food to preserve freshness, e.g.,**
  - – CO_2 diffuses out from bottles
  - – O_2 diffuses into the bottles

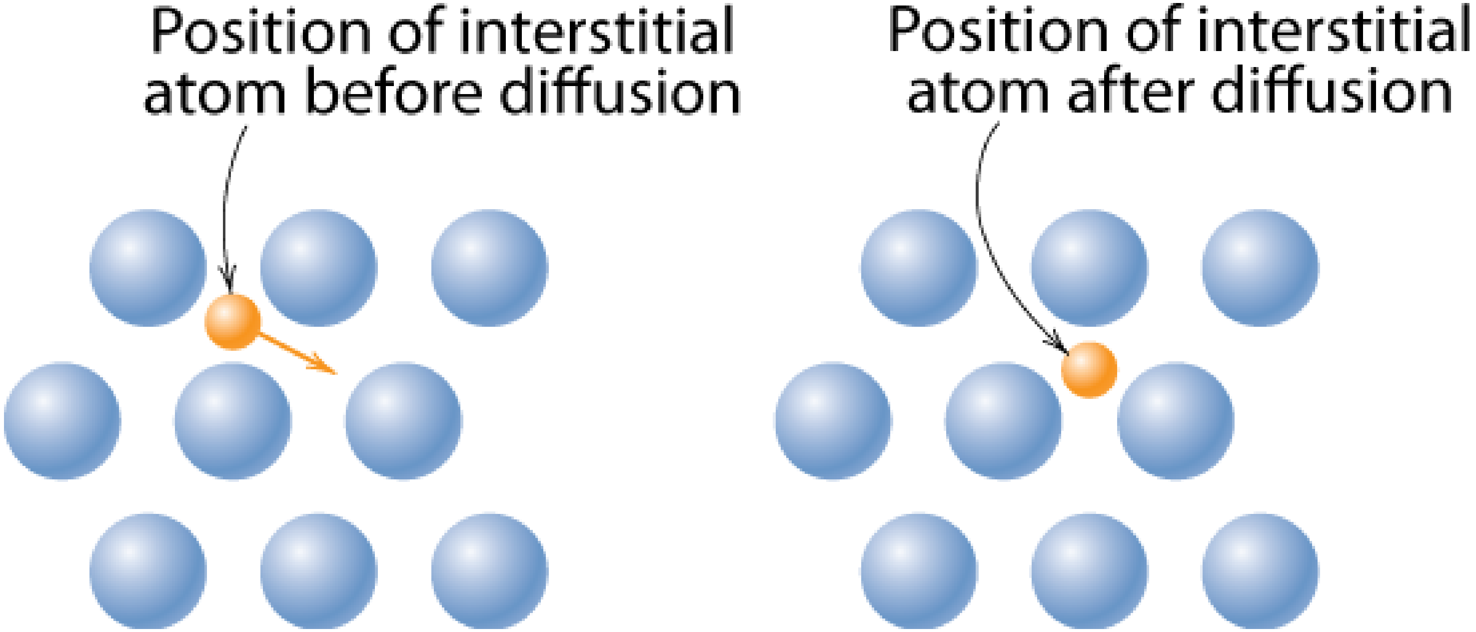
- **Paints applied to metal surface to prevent corrosion**
  - – O_2, H_2O, and salt diffuse through the paint layer (even undamaged) to corrode metals underneath

http://www.core77.com/posts/38703/Disguising-Your-Car-with-Fake-Rust-Looks-Interesting-But-Wont-Prevent-Someone-From-Stealing-It

Diffusion Mechanisms (1)

Interstitial diffusion

Smaller atoms/molecules can diffuse through the interstitial sites between larger atoms/molecules.



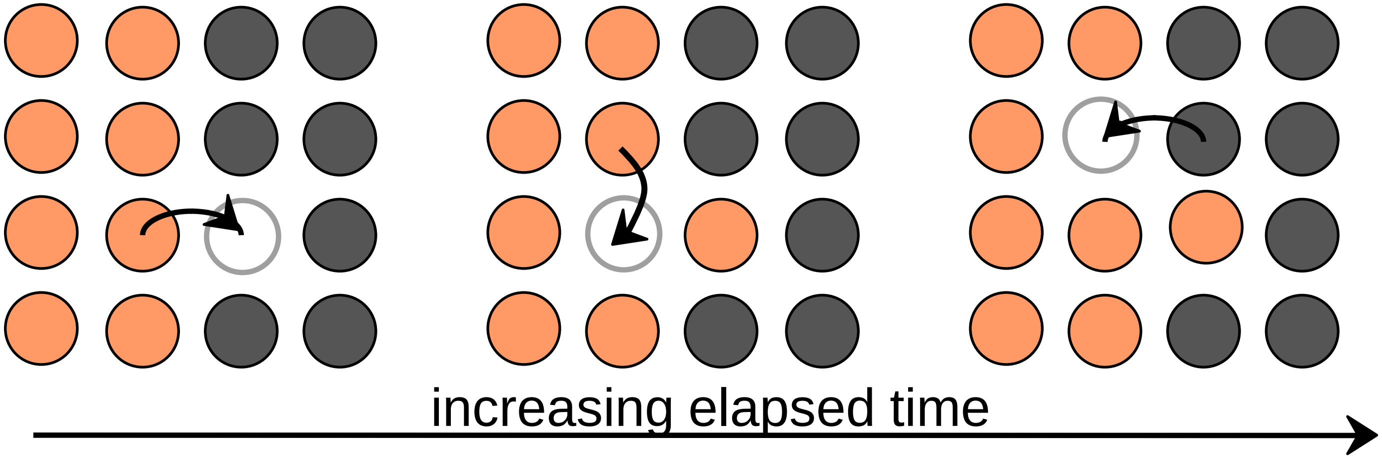
Adapted from Fig. 5.3(b), *Callister & Rethwisch 8e*.

Diffusion Mechanisms (2)

Substitutional Diffusion via vacancy exchange

For pure elements or alloys with similar sized atoms (e.g., Ni-Cu)

- atoms exchange with vacancies
- applies to substitutional impurities atoms and also self diffusion
- rate depends on:
  - -- vacancies concentration
  - -- activation energy to exchange.



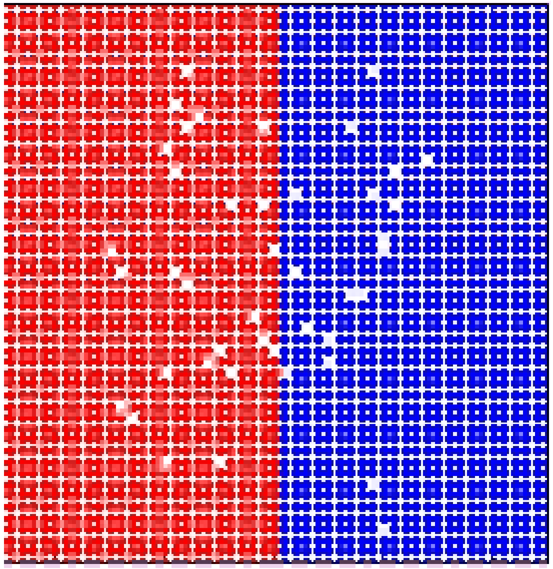
Substitutional diffusion via exchange with vacancy usually much slower than interstitial diffusion

Simulation of Vacancy Diffusion

- Simulation of interdiffusion across an interface:

- Rate of substitutional diffusion depends on:
  - -- vacancy concentration
  - -- frequency of jumping.

This slide contains an animation that requires Quicktime and a Cinepak decompressor. Click on the message or image below to activate the animation.



(Courtesy P.M. Anderson)

Materials Processing Using Diffusion (1)

Example of Case Hardening :
The surface of a metal gear needs to be hard (for wear resistance) while the inside needs to be tough (not brittle)

Approach:

- Diffuse carbon (atoms) into the surface of the steel (iron) gear via heat treatment in an carbon-rich atmosphere
- Carbon atoms are much smaller than Fe atoms – interstitial diffusion mechanism

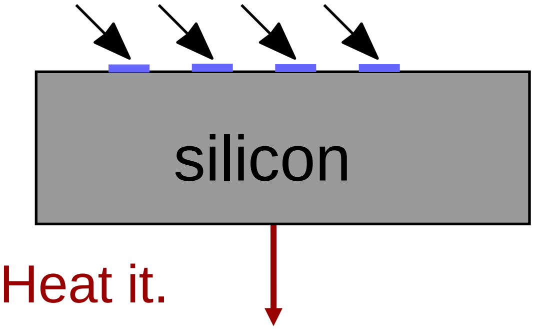
Adapted from chapter-opening photograph, Chapter 5, *Callister & Rethwisch 8e.* (Courtesy of Surface Division, Midland-Ross.)

Result: The presence of C atoms in the surface makes the surface of steel (iron) harder and wear resistant while inside remains low in carbon content and tough (not brittle)

Materials Processing Using Diffusion (2)

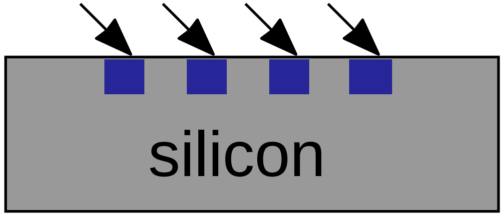
- Doping silicon with phosphorus for *n*-type semiconductors:
- Process:

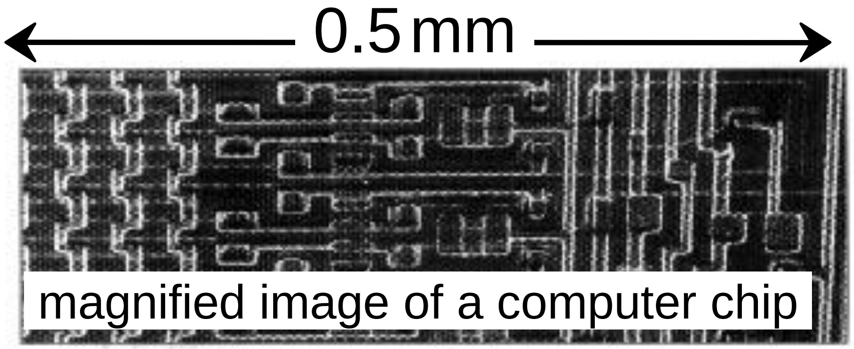
1. Deposit P rich layers on surface.



2. Heat it.

3. Result: Doped semiconductor regions for functional micro-chips





magnified image of a computer chip

light regions: Si atoms

Adapted from Figure 18.27, *Callister & Rethwisch 8e.*

Diffusional Flux

- How do we quantify the amount or rate of diffusion?

$$J \equiv \text{Flux} \equiv \frac{\text{moles (or mass) diffusing}}{(\text{cross-section area})(\text{time})} = \frac{\text{mol}}{\text{cm}^2\text{s}} \text{ or } \frac{\text{kg}}{\text{m}^2\text{s}}$$

$$J = \frac{1}{A}\frac{dM}{dt}$$

Fick's 1st Law about Diffusion

Fick's first law of diffusion for 1D: Flux $\boxed{J = -D\dfrac{dC}{dx}}$

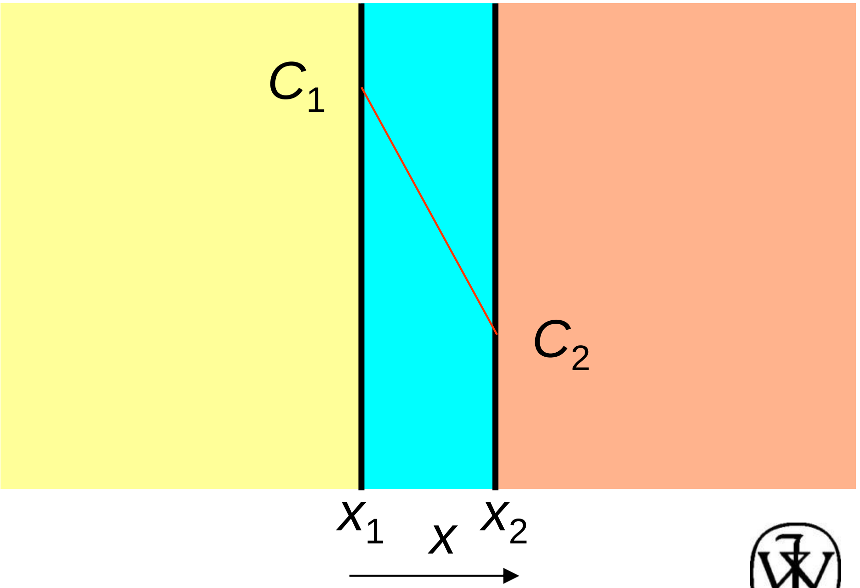
$D \equiv$ **diffusion coefficient**, in unit of **cm²/sec** or similar

C $\equiv$ concentration, in unit of **mole/cm³** or similar

x $\equiv$ distance, in unit of **cm** or similar

dC/*dx* **concentration gradient** along x direction

if linear $\dfrac{dC}{dx} \cong \dfrac{\Delta C}{\Delta x} = \dfrac{C_2 - C_1}{x_2 - x_1}$



Other Example: Chemical Protective Clothing (CPC)

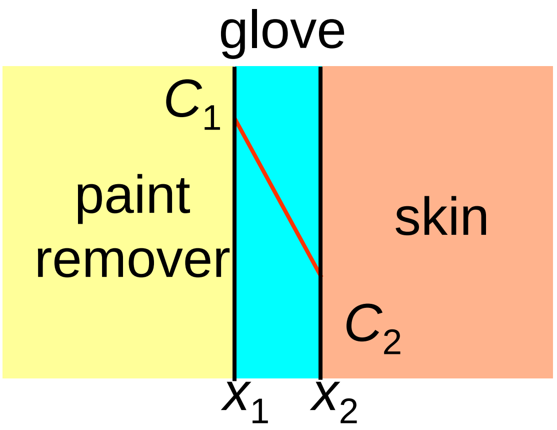
- Methylene chloride is a common ingredient of paint removers. Besides being an irritant, it also may be absorbed through skin. When using this paint remover, protective gloves should be worn.
- If butyl rubber gloves (0.04 cm thick) are used, what is the **diffusive flux** of methylene chloride through the glove if assuming linear concentration distribution?
- Given:
  - diffusion coefficient in butyl rubber:

    $D = 110 \text{x} 10^{-8}$ cm^2/s
  - surface concentrations: C_1 (outside glove) = 0.44 g/cm^3

    C_2 (inside glove) = 0.02 g/cm^3

Example: Chemical Protective Clothing (CPC) (cont).

- Solution –linear conc. gradient



glove

C_1

paint remover

skin

C_2

x_1 x_2

$$J = -D\frac{dC}{dx} \cong -D\frac{C_2 - C_1}{x_2 - x_1}$$

Data: $D = 110\,\text{x}\,10^{-8}\ \text{cm}^2/\text{s}$

$C_1 = 0.44\ \text{g/cm}^3$

$C_2 = 0.02\ \text{g/cm}^3$

$x_2 - x_1 = 0.04\ \text{cm}$ (thickness of glove)

$$J = -(110\,\text{x}\,10^{-8}\ \text{cm}^2/\text{s})\frac{(0.02\ \text{g/cm}^3 - 0.44\ \text{g/cm}^3)}{(0.04\ \text{cm})} = \boxed{1.16\,\text{x}\,10^{-5}\ \frac{\text{g}}{\text{cm}^2\text{s}}}$$

Diffusion Coefficient and Temperature (1)

- Diffusion coefficient increases “exponentially” with increasing temperature T.

$$D = D_o \exp\left(-\frac{Q_d}{RT}\right)$$

D = diffusion coefficient [m^2/s]

D_o = pre-exponential [m^2/s]

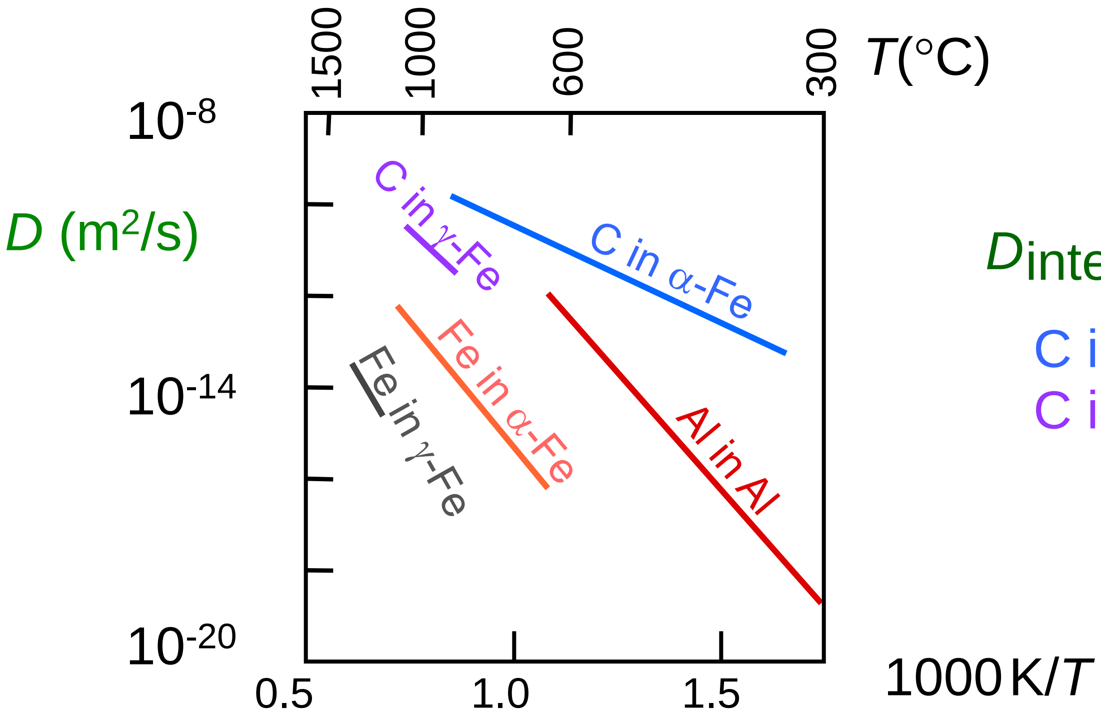
Q_d = activation energy [J/mol]

R = gas constant [8.314 J/mol-K]

T = absolute temperature [K]

Diffusion Coefficient and Temperature (2)

D has "exponential" dependence on *T: higher T* → *much higher D*



$D_{interstitial} >> D_{substitutional}$

$D_{interstitial}$	$D_{substitutional}$
C in α-Fe	Al in Al
C in γ-Fe	Fe in α-Fe
	Fe in γ-Fe

Adapted from Fig. 5.7, *Callister & Rethwisch 8e*. (Date for Fig. 5.7 taken from E.A. Brandes and G.B. Brook (Ed.) *Smithells Metals Reference Book*, 7th ed., Butterworth-Heinemann, Oxford, 1992.)

Example: At 300ºC the diffusion coefficient and activation energy for Cu in Si are

$D_1(300ºC) = 7.8 \times 10^{-11}$ m²/s

$Q_d = 41.5 \times 10^3$ J/mol

What is the diffusion coefficient at 350ºC?

Solution

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

Knowing

$$D_1 = D_0 \exp\left(-\frac{Q_d}{RT_1}\right)$$

Wanting to know

$$D_2 = D_0 \exp\left(-\frac{Q_d}{RT_2}\right)$$

Example (cont.)

$$\frac{D_2}{D_1} = \frac{\exp\left(-\frac{Q_d}{RT_2}\right)}{\exp\left(-\frac{Q_d}{RT_1}\right)}$$

$$D_2 = D_1 \exp\left[-\frac{Q_d}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

$T_1 = 273 + 300 = 573\ \text{K}$

$T_2 = 273 + 350 = 623\ \text{K}$

$$D_2 = (7.8 \text{ x } 10^{-11}\ \text{m}^2/\text{s}) \exp\left[\frac{-41{,}500\ \text{J/mol}}{8.314\ \text{J/mol-K}}\left(\frac{1}{623\ \text{K}} - \frac{1}{573\ \text{K}}\right)\right]$$

$$\boxed{D_2 = 15.7 \text{ x } 10^{-11}\ \text{m}^2/\text{s}}$$

Summary

Diffusion is mass transport by random walking
Of atoms/molecules

Mechanism of diffusion include interstitial diffusion mechanism and vacancy diffusion mechanism

For 1D, Fick's 1st Law gives $J = -D\frac{dC}{dx}$ that relates

diffusion flux *J* and concentration gradient *dC*/*dx* via a material/system property of diffusion coefficient *D*

Diffusion coefficient *D* increases "exponentially" with temperature *T* following

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