DIFFUSION OF SOLIDS

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DIFFUSION IN SOLIDS

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

Diffusion - Mass transport by atomic motion

Mechanisms

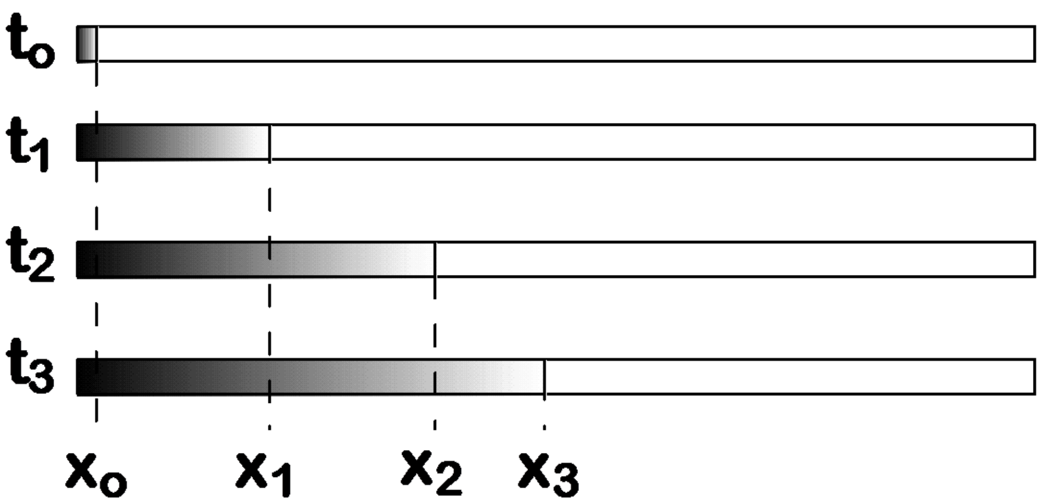
- **Gases & Liquids – random motion**
- **Solids – vacancy diffusion or interstitial diffusion**

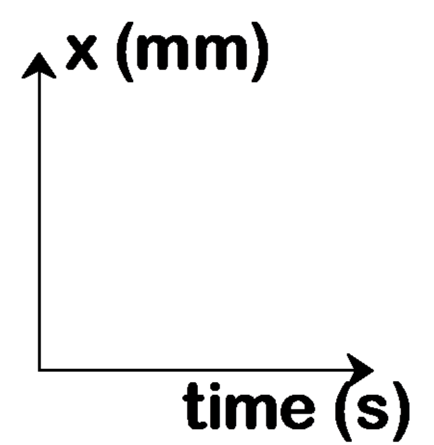
Why Study Diffusion ?

- Diffusion plays a crucial role in…
  - Alloying metals => bronze, silver, gold
  - Strengthening and heat treatment processes
    - Hardening the surfaces of steel
  - High temperature mechanical behavior
  - Phase transformations
    - Mass transport during FCC to BCC
  - Environmental degradation
    - Corrosion, etc.

DIFFUSION DEMO

- **Glass tube filled with water.**
- **At time t = 0, add some drops of ink to one end of the tube.**
- **Measure the diffusion distance, x, over some time.**
- **Compare the results with theory.**



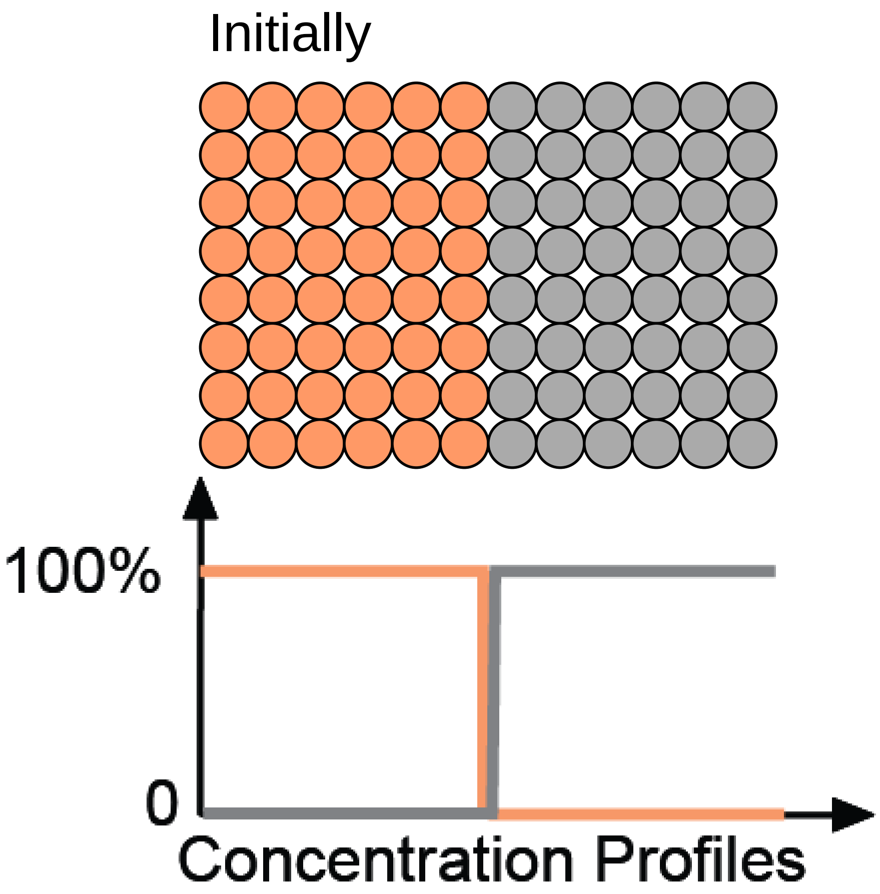


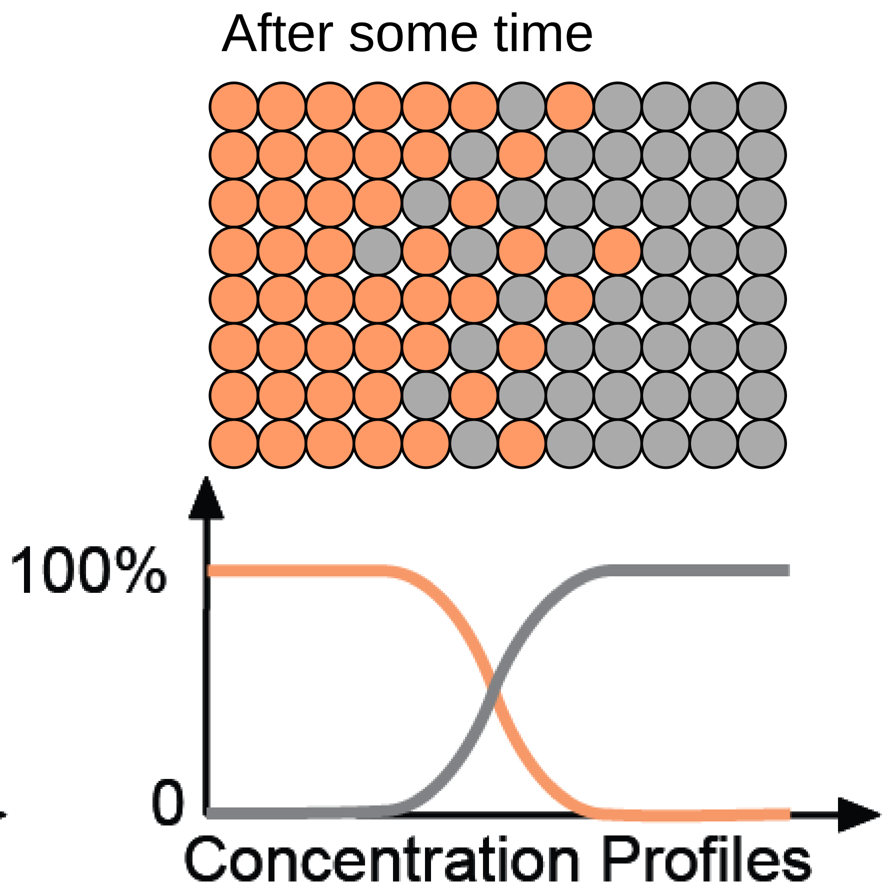
How do atoms move in Solids ?
Why do atoms move in Solids ?

- Diffusion, simply, is atoms moving from one lattice site to another in a stepwise manner
  - Transport of material by moving atoms
- Two conditions are to be met:
  - An empty adjacent site
  - Enough energy to break bonds and cause lattice distortions during displacement
- What is the energy source ?
  - HEAT !
- What else ?
  - **Concentration gradient !**

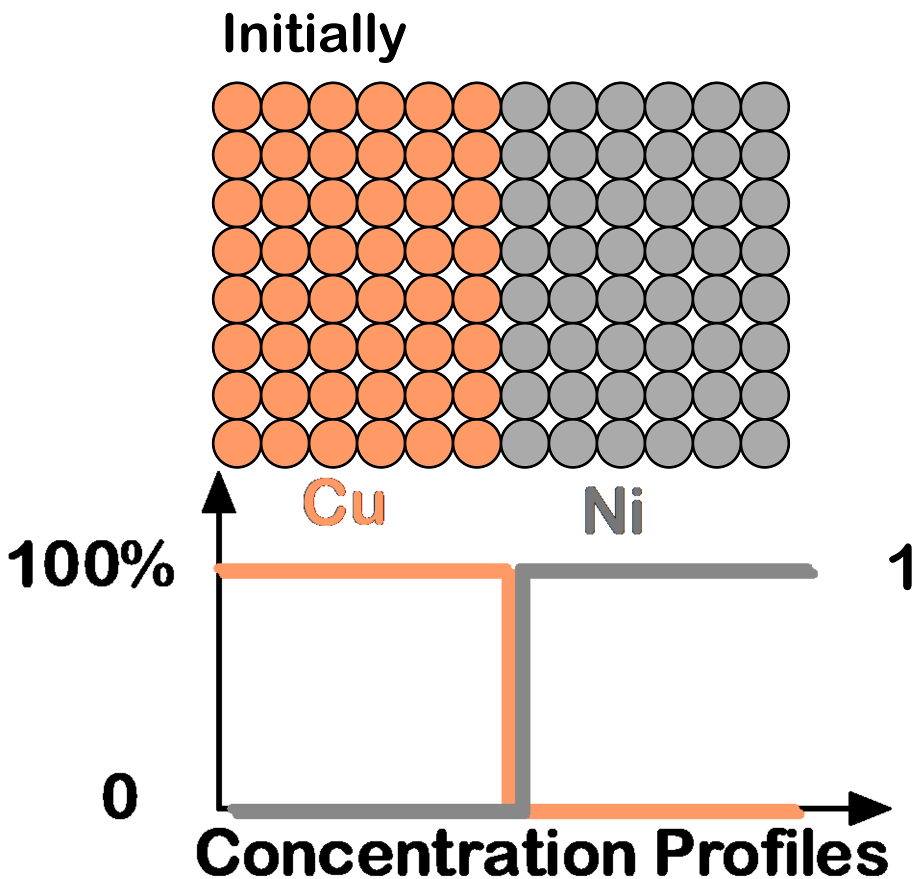
Diffusion

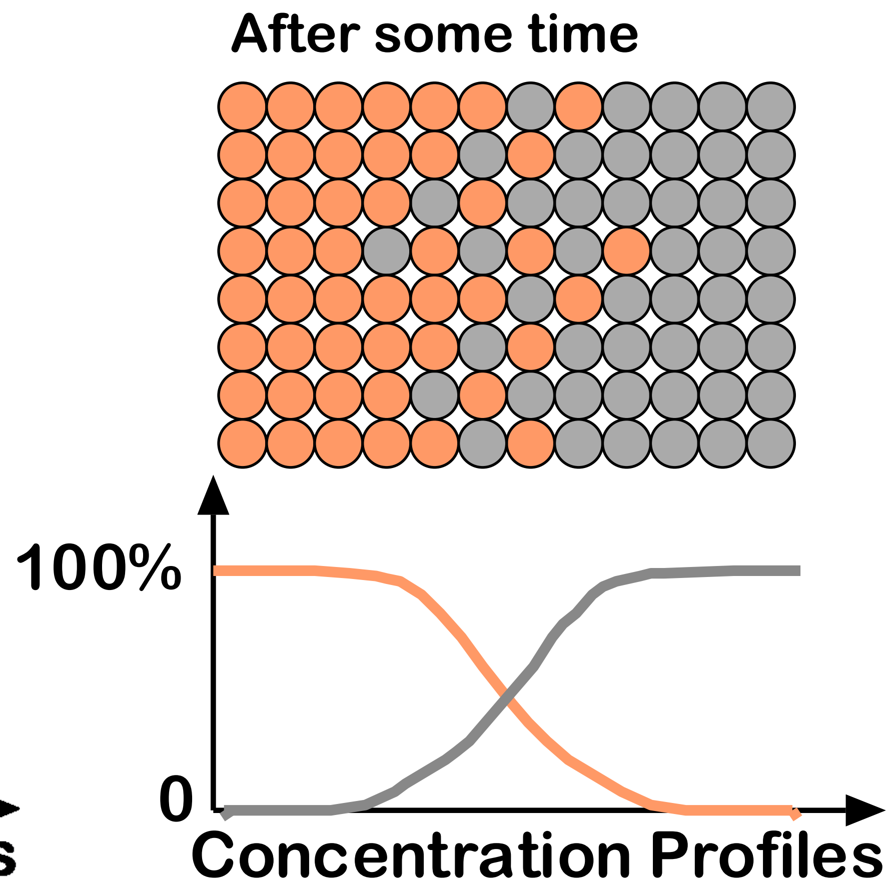
- Interdiffusion: In an alloy, atoms tend to migrate from regions of high conc. to regions of low conc.





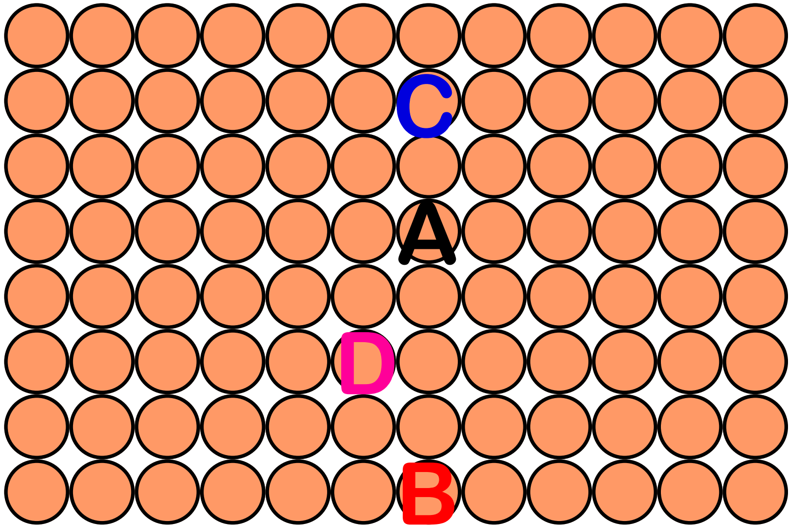
• **Interdiffusion**: In an alloy, atoms tend to migrate from regions of large concentration.



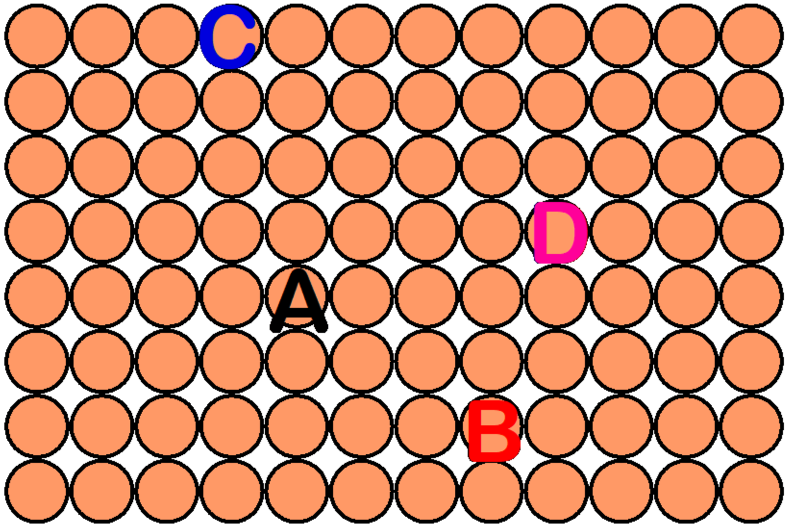


- **Self-diffusion**: **In an elemental solid, atoms also migrate.**

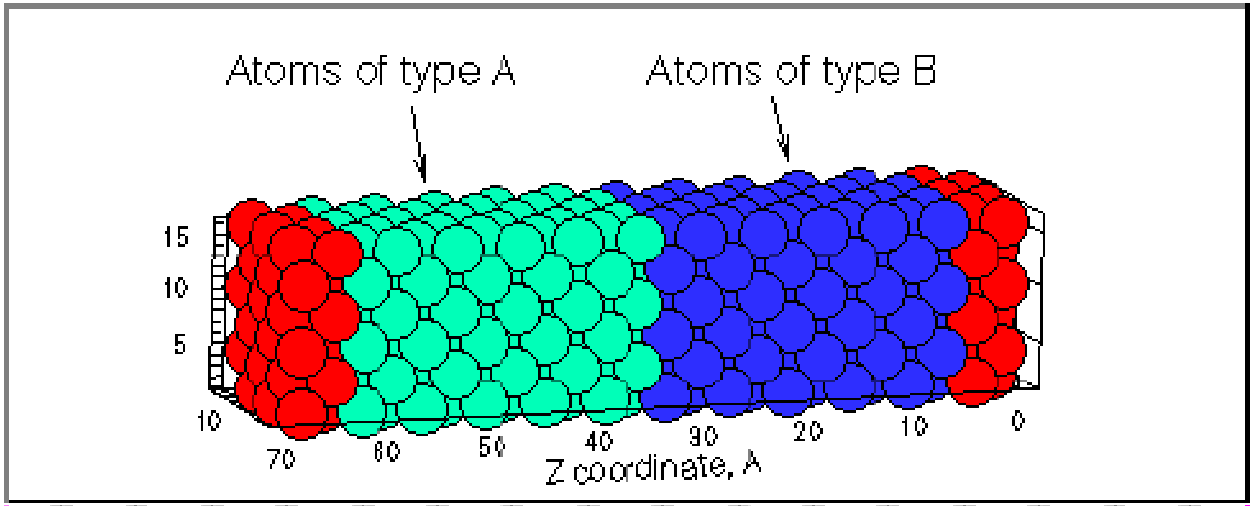
Label some atoms (use isotopes)

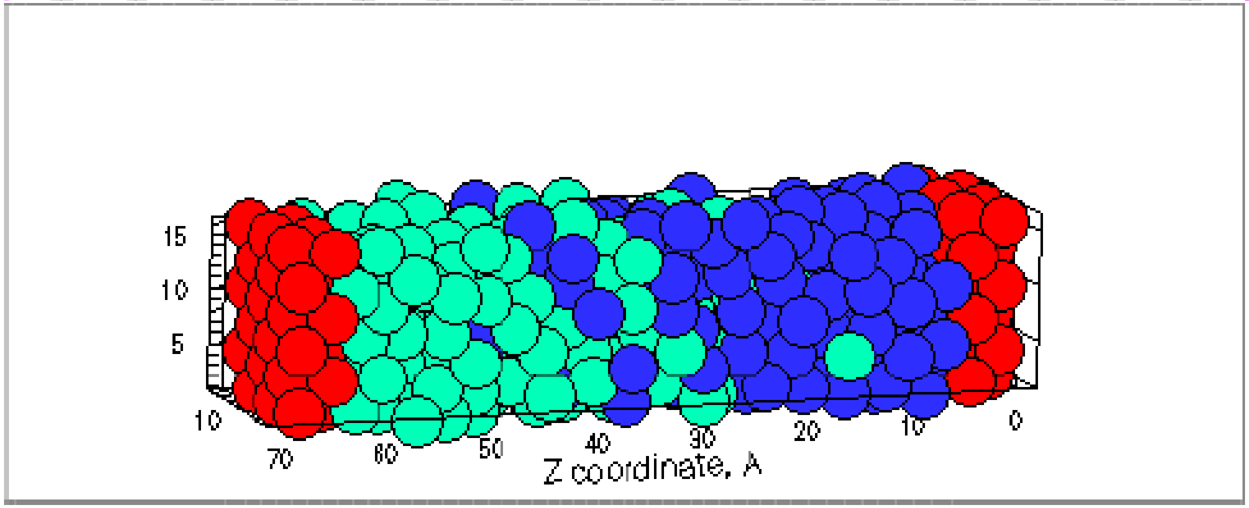


After some time



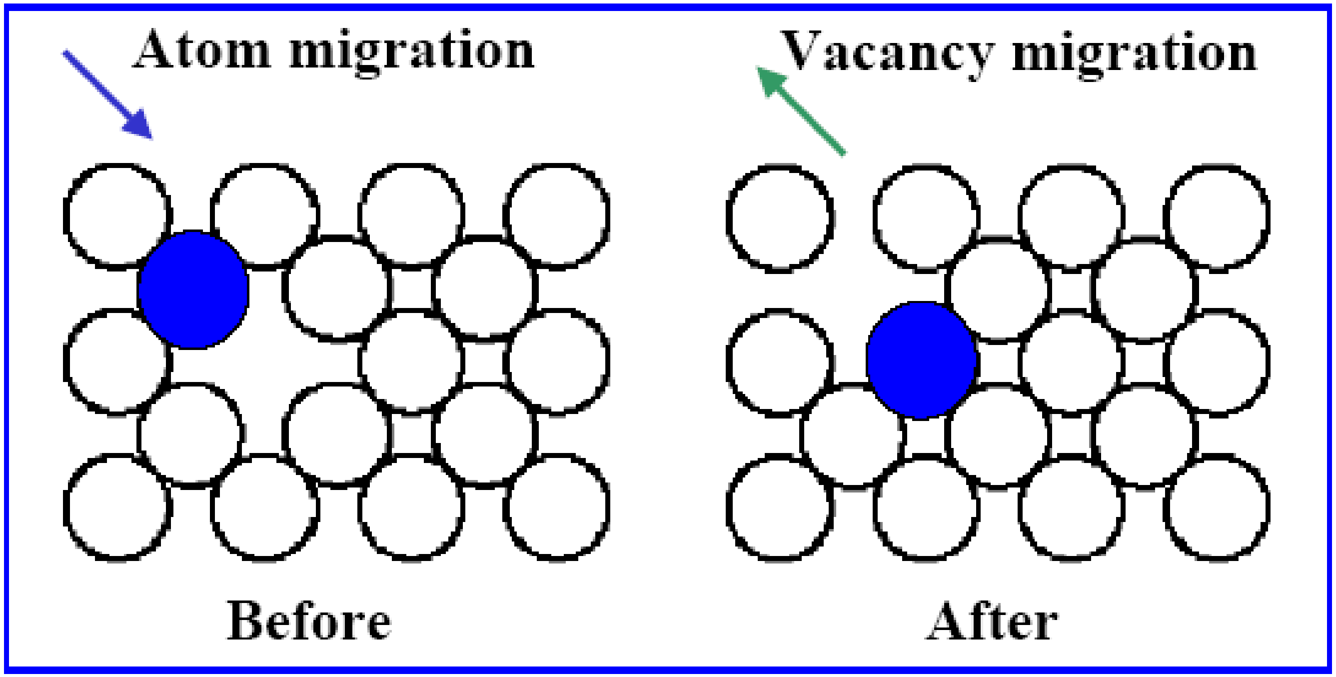
More examples in 3-D !





Diffusion Mechanisms

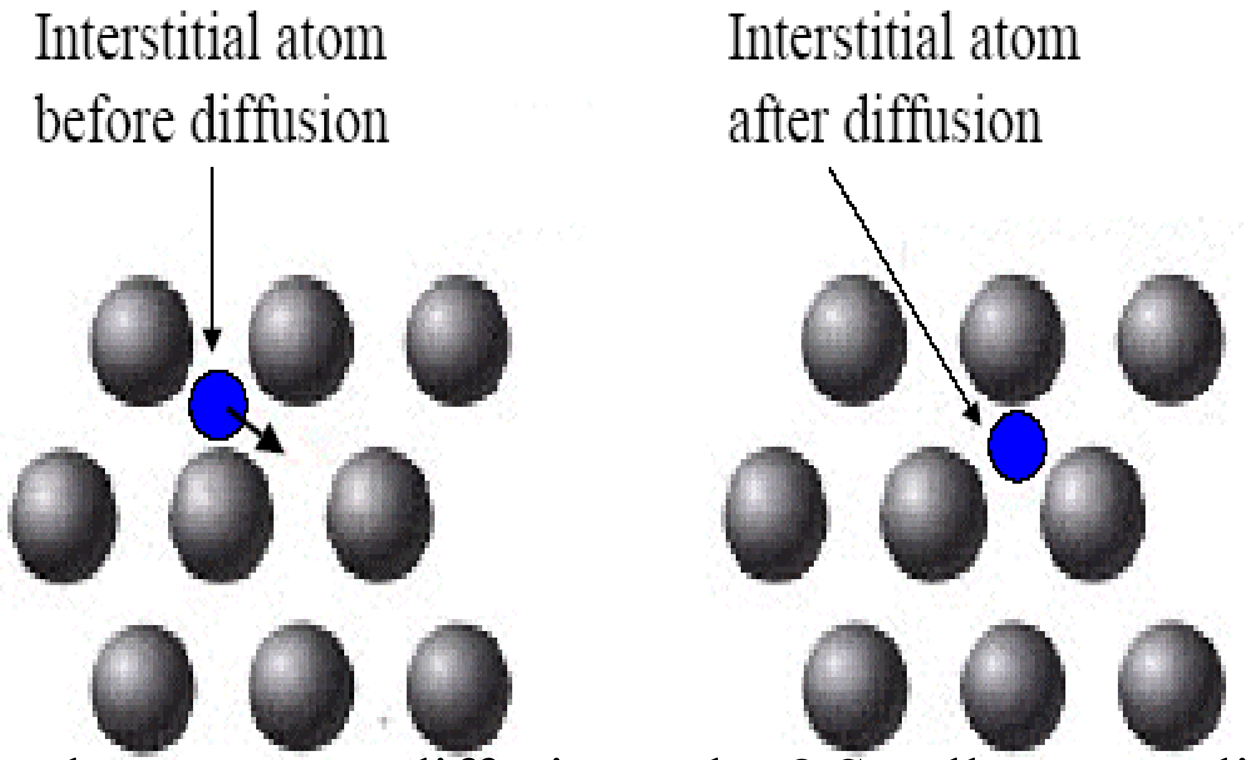
Vacancy diffusion



Energy is needed to generate a vacancy, break bonds, cause distortions. Provided by HEAT , kT !
Atom moves in the opposite direction of the vacancy !

Diffusion Mechanisms (II)

Interstitial Diffusion

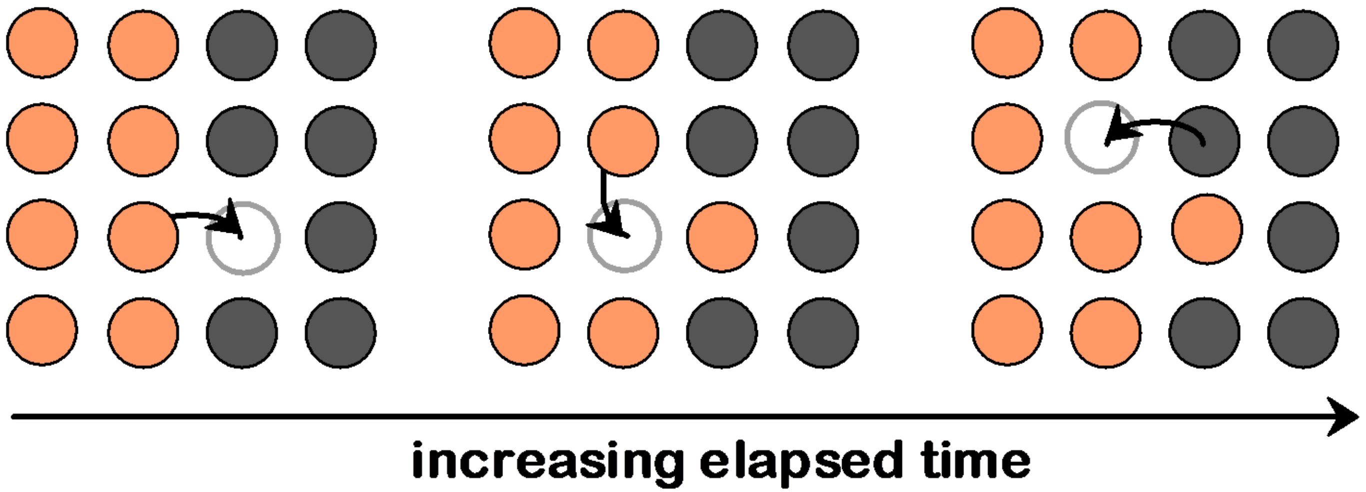


Much faster than vacancy diffusion, why ? Smaller atoms like B, C, H, O. Weaker interaction with the larger atoms. More vacant sites, no need to create a vacancy !

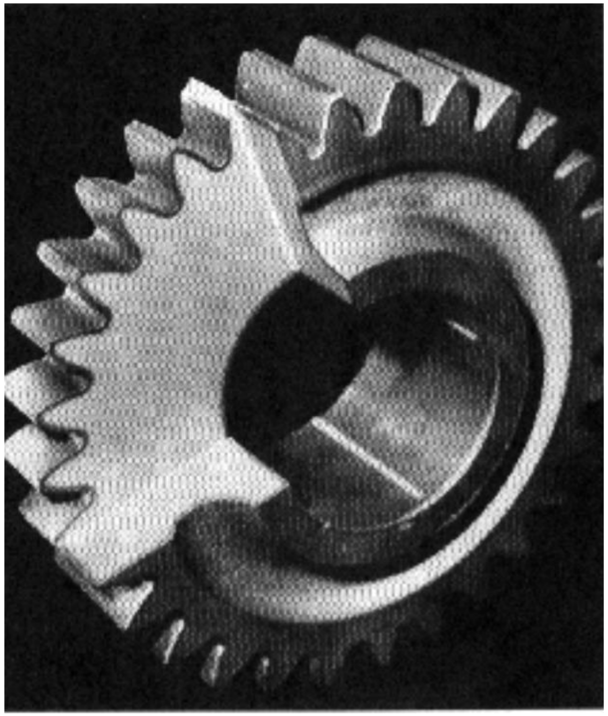
Diffusion Mechanisms (III)

Substitutional Diffusion:

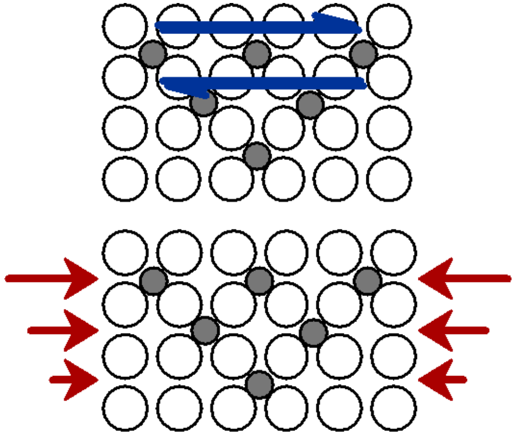
- **applies to substitutional impurities**
- **atoms exchange with vacancies**
- **rate depends on:**
  - **--number of vacancies**
  - **--activation energy to exchange.**



- Case Hardening:
  --Diffuse carbon atoms into the host iron atoms at the surface.
  --Example of interstitial diffusion is a case hardened gear.



- Result: The "Case" is
  --hard to deform: C atoms "lock" planes from shearing.
  --hard to crack: C atoms put the surface in compression.



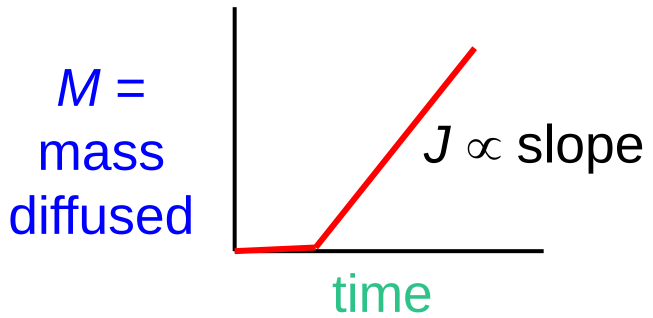
Diffusion

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

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

- Measured empirically
  - Make thin film (membrane) of known surface area
  - Impose concentration gradient
  - Measure how fast atoms or molecules diffuse through the membrane

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



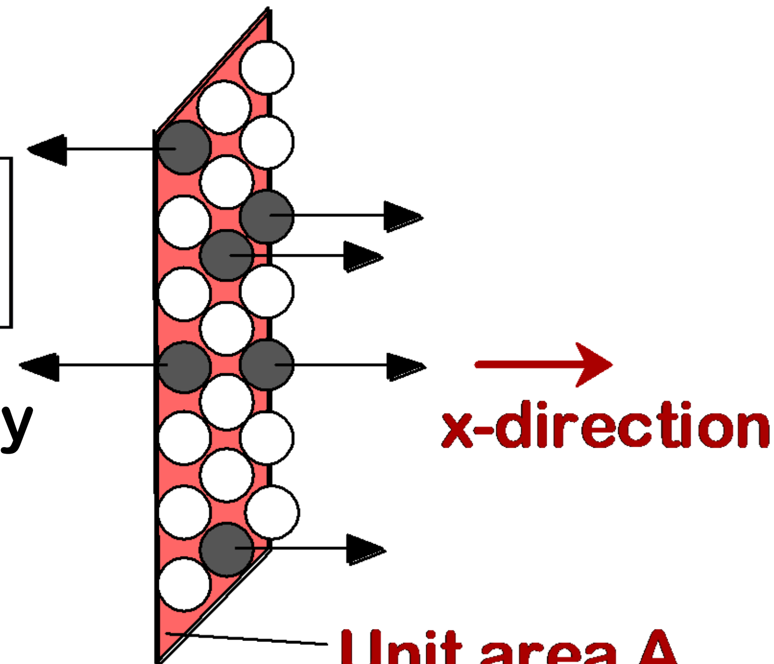
MODELING DIFFUSION: FLUX

RATE OF MATERIAL TRANSPORT

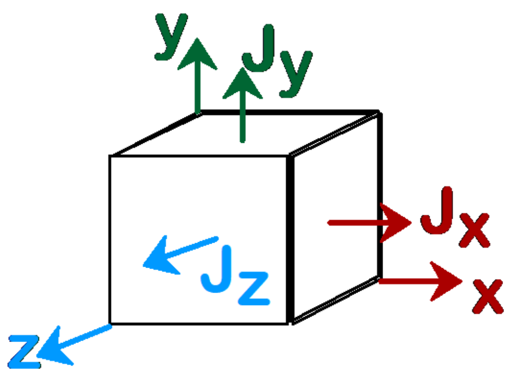
- **Diffusion Flux:**

Material

$$J = \frac{1}{A}\frac{dM}{dt} \Rightarrow \left[\frac{\text{kg}}{\text{m}^2\text{s}}\right] \text{ or } \left[\frac{\text{atoms}}{\text{m}^2\text{s}}\right]$$



- **Directional Quantity (anisotropy ?)**

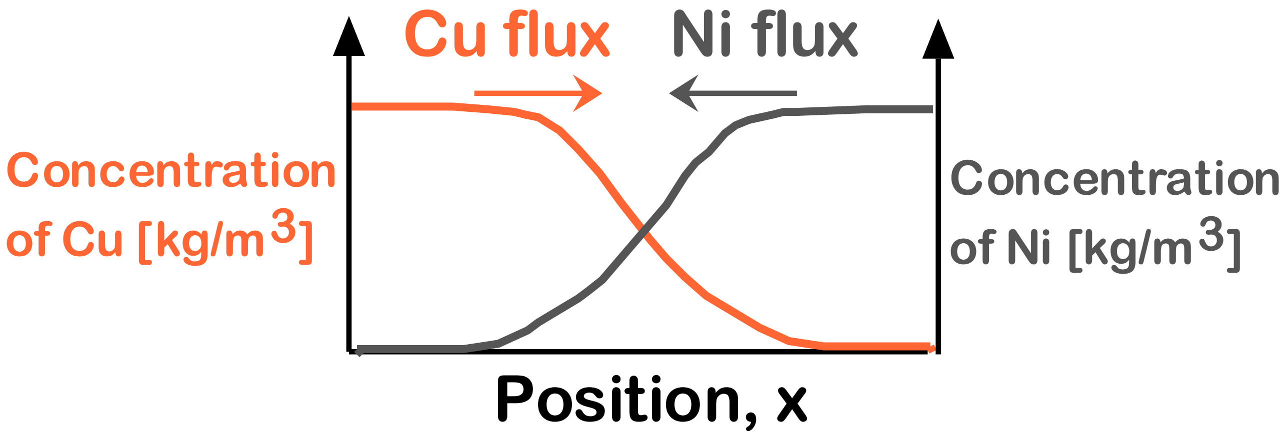


- **Flux can be measured for:**
  - --vacancies
  - --host (A) atoms
  - --impurity (B) atoms

Diffusion is a time-dependent process !

CONCENTRATION PROFILES & FLUX

- **Concentration Profile**, C(x): [kg/m^3]



Adapted from Fig. 5.2(c), *Callister 6e*.

- **Fick's First Law:**

$$J_x = -D\frac{dC}{dx}$$

flux in x-dir. [kg/m^2-s] → J_x

Diffusion coefficient [m^2/s] → D

concentration gradient [kg/m^4] → $\frac{dC}{dx}$

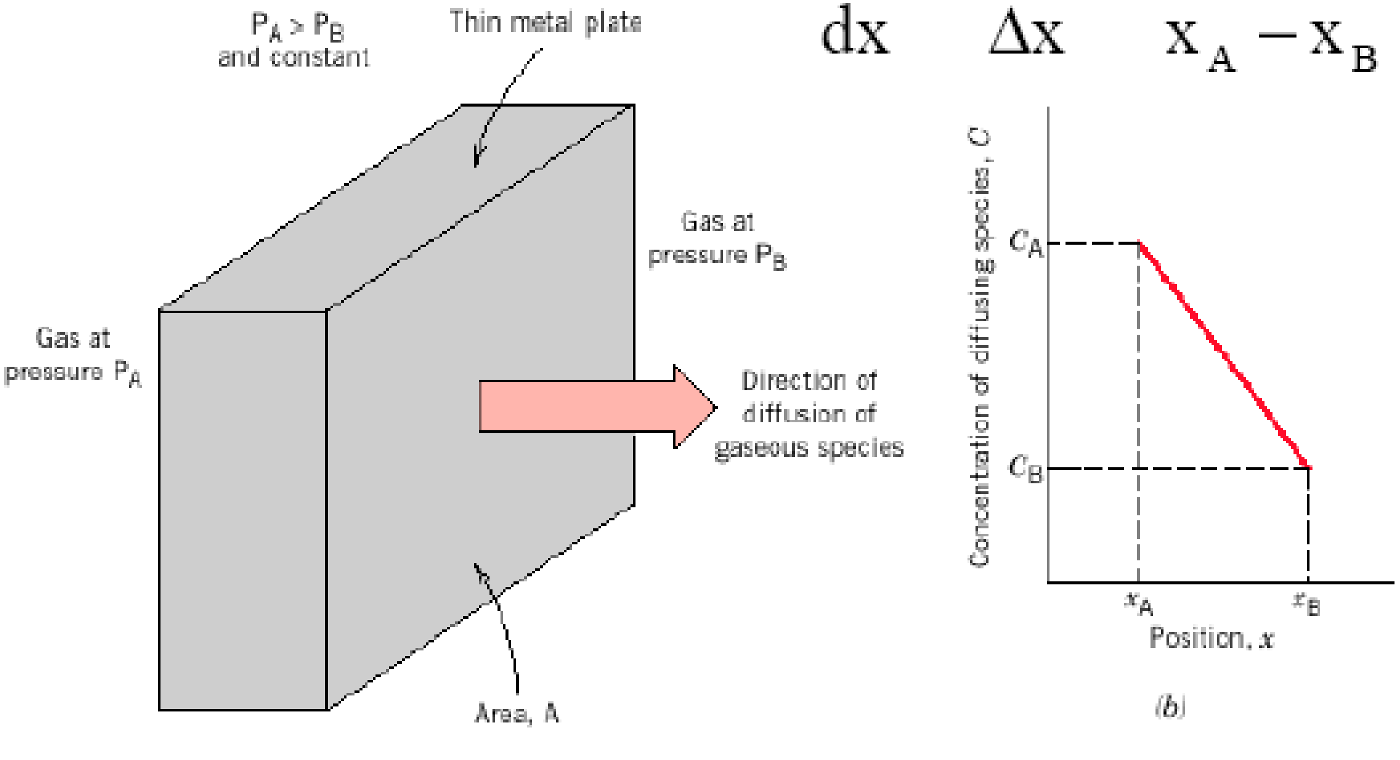
- **The steeper the concentration profile, the greater the flux!**

Concentration gradient is the DRIVING FORCE !

Concentration Gradient

Concentration gradient: dC/dx (Kg.m^{-3}): the slope at a particular point on concentration profile.

$$\frac{dC}{dx} \cong \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$$

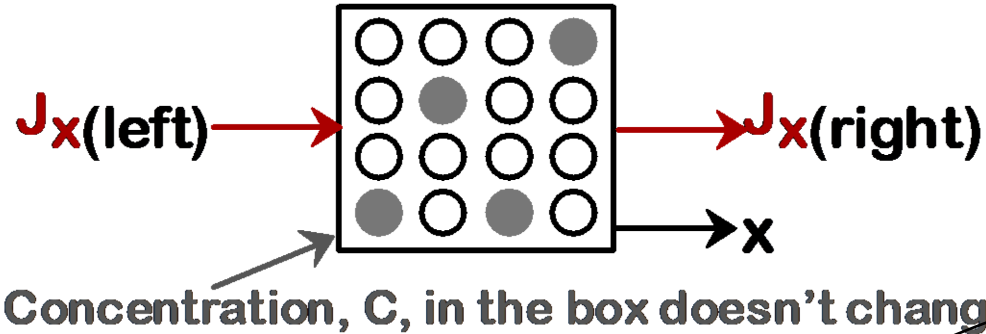


(a)

(b)

STEADY STATE DIFFUSION

- **Steady State**: **the concentration profile doesn't change with time.**



Steady State:

$J_x(\text{left}) = J_x(\text{right})$

- **Apply Fick's First Law:** $J_x = -D \dfrac{dC}{dx}$

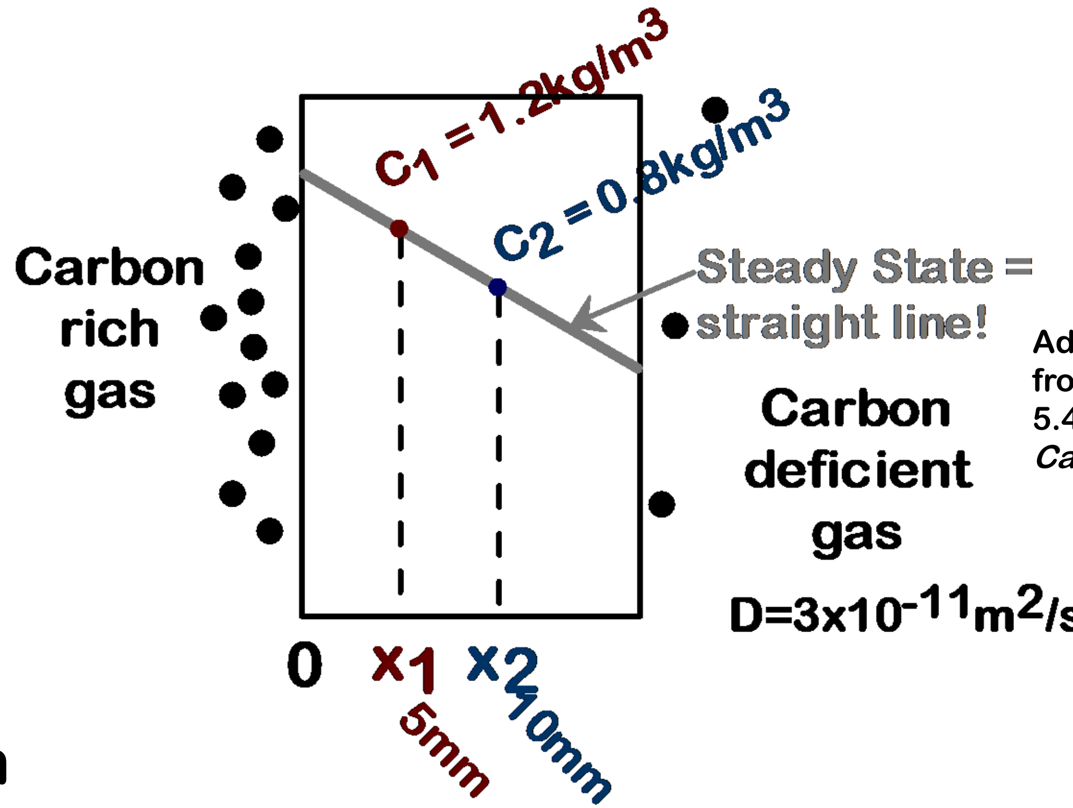
Why is the minus sign ?

- **If** $J_x)_{\text{left}} = J_x)_{\text{right}}$ **, then** $\left(\dfrac{dC}{dx}\right)_{\text{left}} = \left(\dfrac{dC}{dx}\right)_{\text{right}}$

- **Result: the slope, dC/dx, must be constant (i.e., slope doesn't vary with position)!**

EX: STEADY STATE DIFFUSION

- Steel plate at 700° C



Adapted from Fig. 5.4, *Callister 6e*.

- Q: How much carbon transfers from the rich to the deficient side?

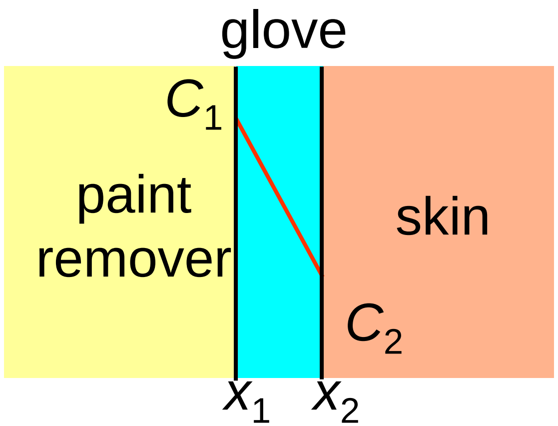
$$J = -D \frac{C_2 - C_1}{x_2 - x_1} = 2.4 \times 10^{-9} \frac{kg}{m^2 s}$$

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?**
- **Data:**
  - **diffusion coefficient in butyl rubber:** $D = 110 \times 10^{-8}\ \text{cm}^2/\text{s}$
  - **surface concentrations:** $C_1 = 0.44\ \text{g/cm}^3$ $C_2 = 0.02\ \text{g/cm}^3$

Example (cont).

- Solution – assuming linear conc. gradient



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

Data:

$D = 110 \times 10^{-8}\ \text{cm}^2/\text{s}$

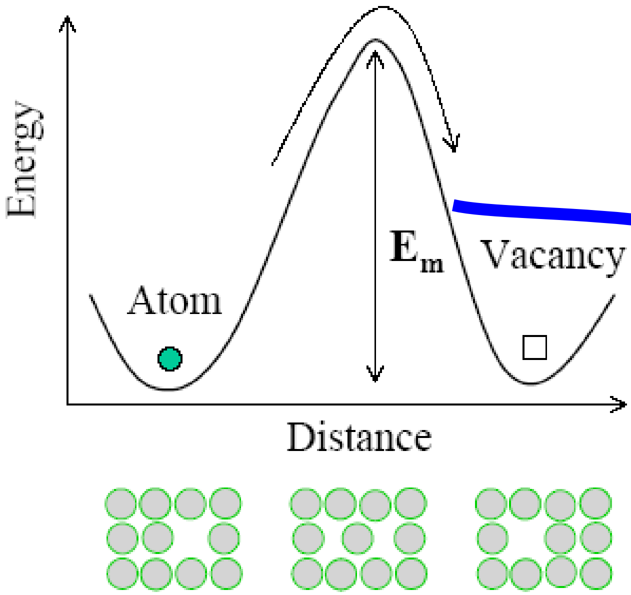
$C_1 = 0.44\ \text{g/cm}^3$

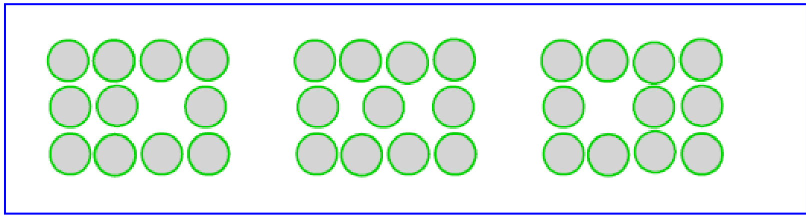
$C_2 = 0.02\ \text{g/cm}^3$

$x_2 - x_1 = 0.04\ \text{cm}$

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

Temperature Dependency !





What is the probability to find a vacancy at a nearest site ?

$$\exp\left(-\,Q_v \big/ k_B T\right)$$

Atom has to break bonds and "squeeze" thru => activation energy, $E_m \approx 1$ eV .

$$R_j = R_0 \exp\left(-\,E_m \big/ k_B T\right)$$

COMBINE

Diffusion and Temperature

- Diffusion coefficient increases with increasing T.

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

D = diffusion coefficient [m^2/s]

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

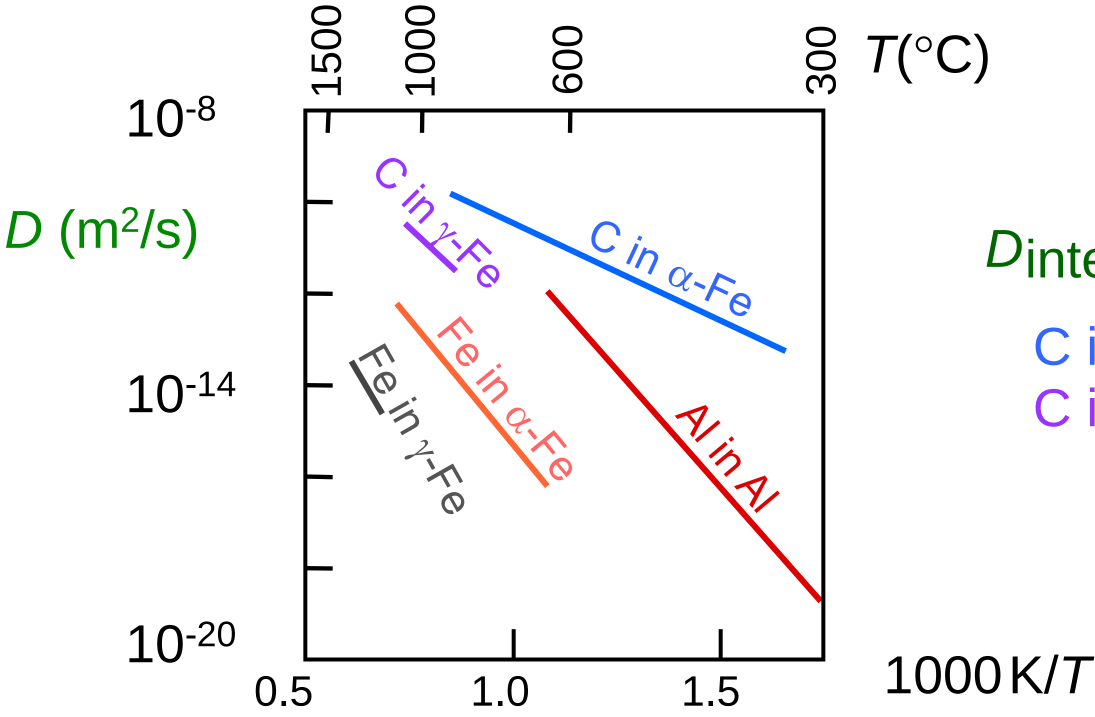
Q_d = activation energy [J/mol or eV/atom]

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

T = absolute temperature [K]

Diffusion and Temperature

D has exponential dependence on *T*



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

C in α-Fe	Al in Al
C in γ-Fe	Fe in α-Fe
	Fe in γ-Fe

DIFFUSION AND TEMPERATURE

- Diffusivity increases with T.

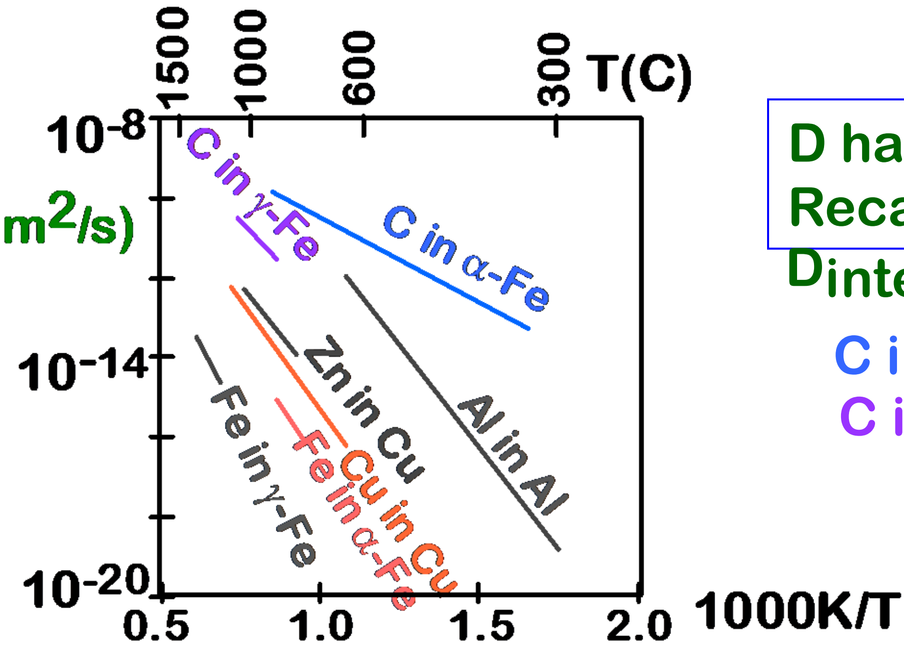
pre-exponential [m²/s] (see Table 5.2, *Callister 6e*)

activation energy [J/mol],[eV/mol] (see Table 5.2, *Callister 6e*)

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

gas constant [8.31J/mol-K]

- Experimental Data:



D has exp. dependence on T
Recall: Vacancy does also!

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

C in α-Fe
C in γ-Fe

Cu in Cu
Al in Al
Fe in α-Fe
Fe in γ-Fe
Zn in Cu

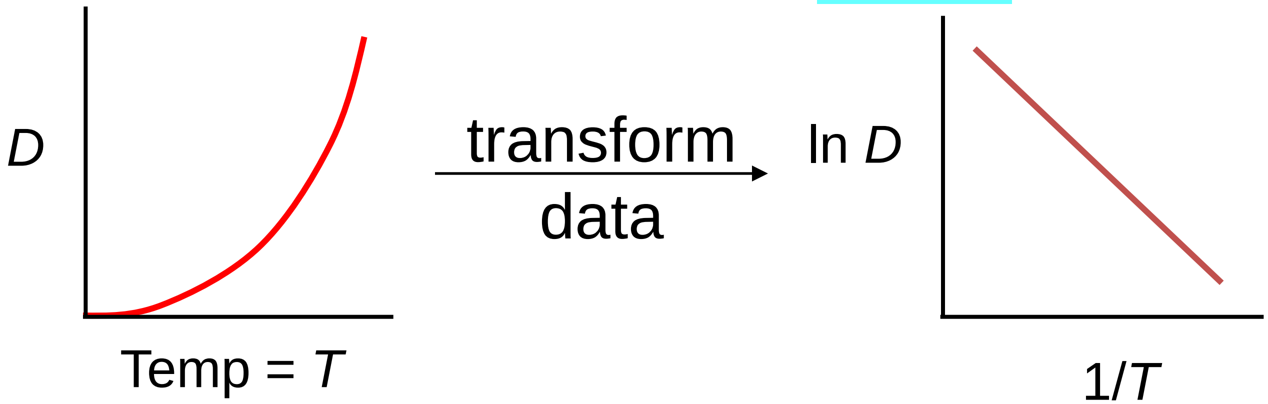
Example: At 300ºC the diffusion coefficient and activation energy for Cu in Si are

$D(300ºC) = 7.8 \times 10^{-11}\ m^2/s$

$Q_d = 41.5$ kJ/mol

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

What is the diffusion coefficient at 350ºC?



$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_2}\right) \quad \text{and} \quad \ln D_1 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_1}\right)$$

$$\therefore \quad \ln D_2 - \ln D_1 = \ln\frac{D_2}{D_1} = -\frac{Q_d}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Example (cont.)

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

$$T_1 = 273 + 300 = 573\,K$$

$$T_2 = 273 + 350 = 623\,K$$

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

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

Fick's Second Law ; Non-steady state Diffusion

- In most practical cases, J (flux) and dC/dx (concentration gradient) change with time (t).
  - Net accumulation or depletion of species diffusing
- How do we express a time dependent concentration?

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} \right) = D \frac{\partial^2 C}{\partial x^2}$$

Concentration at a point *x* Changing with time

?

Flux, J, changes at any point *x* !

How do we solve this partial differential equation ?

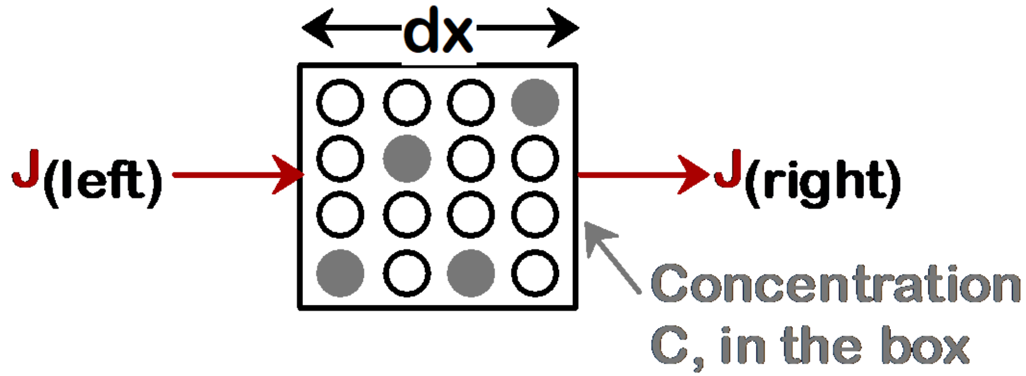
$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x} \right) = D \frac{\partial^2 C}{\partial x^2}$$

- Use proper boundary conditions:
  - $t=0$, $C = C_0$, at $0 \leq x \leq \infty$
  - $t>0$, $C = C_s$, at $x = 0$

    $C = C_0$, at $x = \infty$

NON STEADY STATE DIFFUSION

- Concentration profile, C(x), changes w/ time.



- To conserve matter:

$$\frac{J(\text{right}) - J(\text{left})}{dx} = -\frac{dC}{dt}$$

$$\frac{dJ}{dx} = -\frac{dC}{dt}$$

- Fick's First Law:

$$J = -D\frac{dC}{dx} \quad \text{or}$$

$$\frac{dJ}{dx} = -D\frac{d^2C}{dx^2} \quad \text{(if D does not vary with x)}$$

equate

- Governing Eqn.:

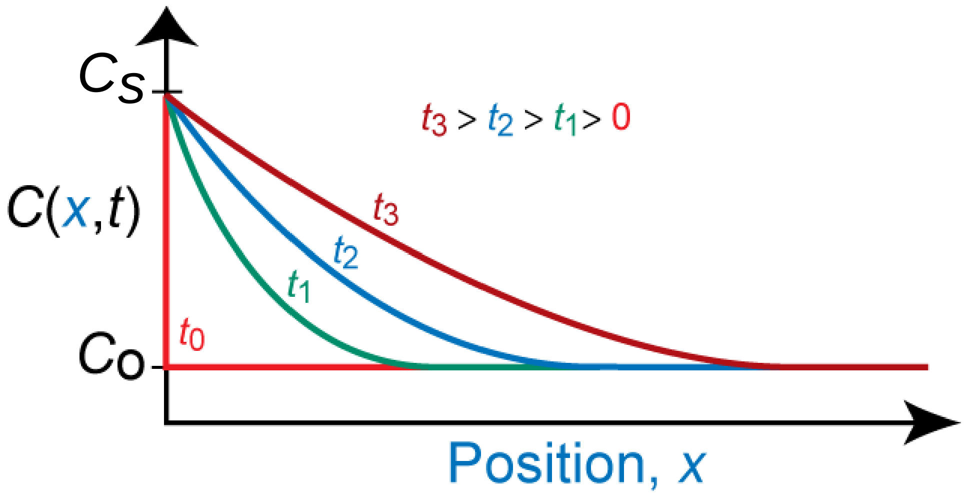
$$\frac{dC}{dt} = D\frac{d^2C}{dx^2}$$

Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.

Surface conc., C_S of Cu atoms

pre-existing conc., C_o of copper atoms



Adapted from Fig. 5.5, *Callister 7e*.

B.C. at $t = 0$, $C = C_o$ for $0 \leq x \leq \infty$

at $t > 0$, $C = C_S$ for $x = 0$ (const. surf. conc.)

$C = C_o$ for $x = \infty$

Solution:

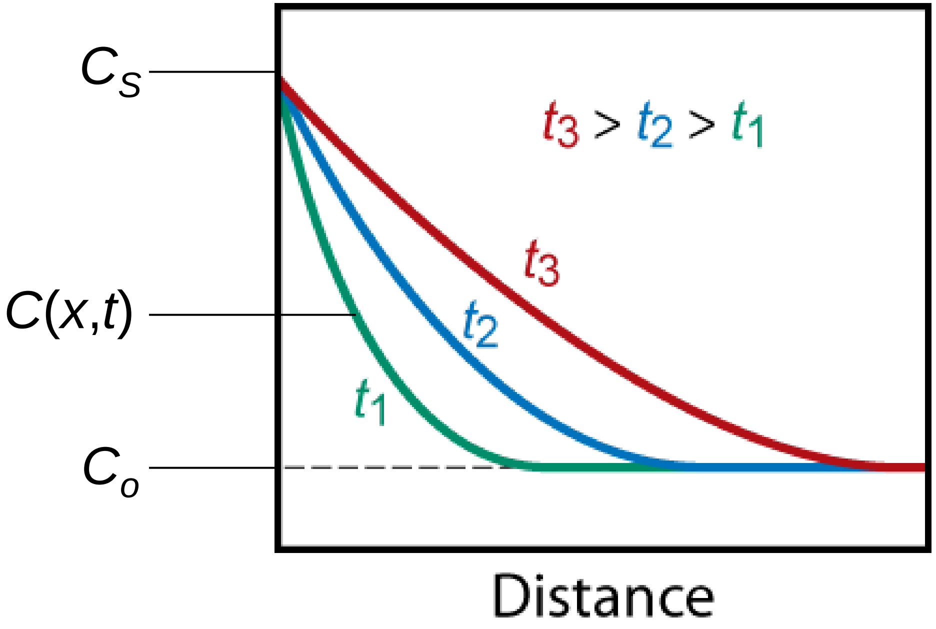
$$\frac{C(x,t)-C_o}{C_s-C_o}=1-\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$C(x,t)$ = Conc. at point x at time t

erf (z) = error function

$$=\frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}dy$$

erf(z) values are given in Table 6.2



Non-steady State Diffusion

- **Sample Problem: An FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere that gives a surface carbon concentration constant at 1.0 wt%. If after 49.5 h the concentration of carbon is 0.35 wt% at a position 4.0 mm below the surface, determine the temperature at which the treatment was carried out.**

$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

- **Solution:**

Solution (cont.):

$$\frac{C(x,t)-C_o}{C_s-C_o}=1-\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

- t = 49.5 h
- C_x = 0.35 wt%
- C_o = 0.20 wt%

x = 4 x 10^{-3} m

C_s = 1.0 wt%

$$\frac{C(x,t)-C_o}{C_s-C_o}=\frac{0.35-0.20}{1.0-0.20}=1-\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)=1-\text{erf}(z)$$

$\therefore$ erf(z) = 0.8125

Solution (cont.):

We must now determine from Table 5.1 the value of *z* for which the error function is 0.8125. An interpolation is necessary as follows

z	erf(z)
0.90	0.7970
z	0.8125
0.95	0.8209

$$\frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}$$

$$z = 0.93$$

Now solve for *D*

$$z = \frac{x}{2\sqrt{Dt}} \Rightarrow D = \frac{x^2}{4z^2 t}$$

$$\therefore D = \left(\frac{x^2}{4z^2 t}\right) = \frac{(4 \text{ x } 10^{-3}\text{ m})^2}{(4)(0.93)^2(49.5 \text{ h})} \frac{1 \text{ h}}{3600 \text{ s}} = 2.6 \text{ x } 10^{-11} \text{ m}^2/\text{s}$$

Solution (cont.):

from Table 5.2, for diffusion of C in FCC Fe

D_o = 2.3 x 10^{-5} m^2/s Q_d = 148,000 J/mol

$$T = \frac{Q_d}{R(\ln D_o - \ln D)}$$

$$\therefore \quad T = \frac{148{,}000 \text{ J/mol}}{(8.314 \text{ J/mol-K})(\ln 2.3\text{x}10^{-5} \text{ m}^2/\text{s} - \ln 2.6\text{x}10^{-11} \text{ m}^2/\text{s})}$$

T = 1300 K = 1027°C

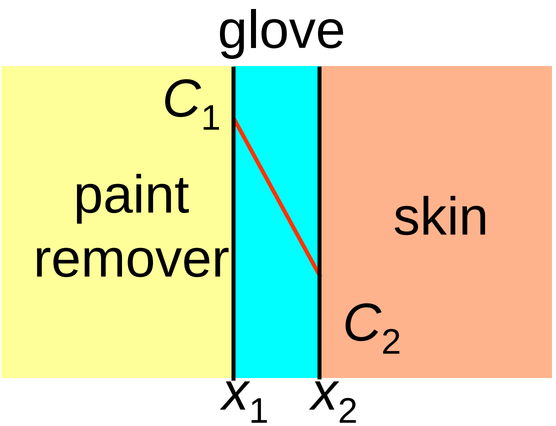
Example: Chemical Protective Clothing (CPC)

- **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 breakthrough time *(t_b)*, i.e., how long could the gloves be used before methylene chloride reaches the hand?**
- **Data (from Table 22.5)**
  - **diffusion coefficient in butyl rubber:**

$$D = 110 \times 10^{-8}\ cm^2/s$$

Example (cont).

- Solution – assuming linear conc. gradient



Equation 22.24 **Given in web chapters !**

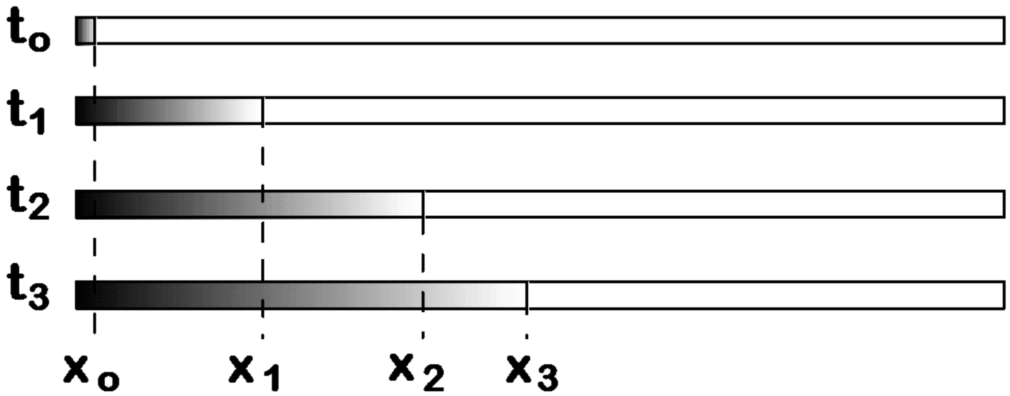
D = 110 x 10^{-8} cm^2/s

$$t_b = \frac{(0.04\ \text{cm})^2}{(6)(110 \times 10^{-8}\ \text{cm}^2/\text{s})} = 240\ \text{s} = \boxed{4\ \text{min}}$$

Time required for breakthrough ca. 4 min

DIFFUSION DEMO: ANALYSIS

- **The experiment: we recorded combinations of t and x that kept C constant.**

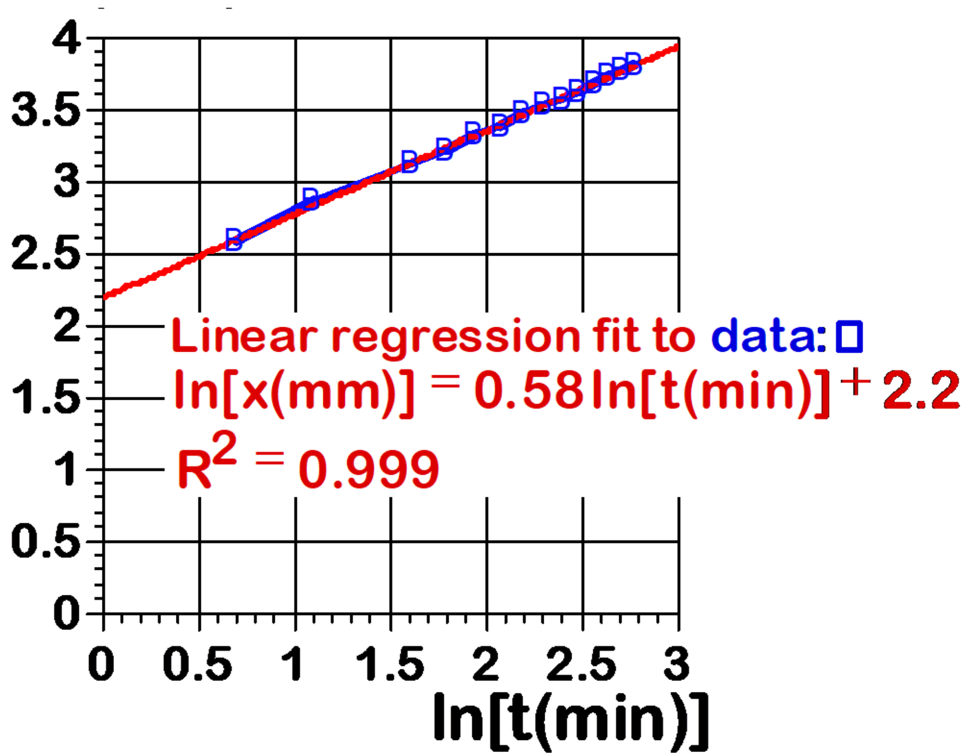


$$\frac{C(x_i, t_i) - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x_i}{2\sqrt{Dt_i}}\right)$$ **= (constant here)**

- **Diffusion depth given by:**

$$x_i \propto \sqrt{Dt_i}$$

DATA FROM DIFFUSION DEMO



- **Experimental result: $x \sim t^{0.58}$**
- **Theory predicts $x \sim t^{0.50}$**
- **Reasonable agreement!**

- Copper diffuses into a bar of aluminum.
- 10 hours at 600C gives desired C(x).
- How many hours would it take to get the same C(x) if we processed at 500C?

Key point 1: $C(x,t_{500C}) = C(x,t_{600C})$.

Key point 2: Both cases have the same C_o and C_s.

- Result: Dt should be held constant.

$$\frac{C(x,t)-C_o}{C_s-C_o} = 1-\text{erf}\left(\frac{x}{\sqrt{2Dt}}\right) \longrightarrow (Dt)_{500°C} = (Dt)_{600°C}$$

- Answer:

$$t_{500} = \frac{(Dt)_{600}}{D_{500}} = 110\text{hr}$$

$D_{600} = 5.3 \times 10^{-13} m^2/s$; $t_{600} = 10$ hrs; $D_{500} = 4.8 \times 10^{-14} m^2/s$

Note: values of D are provided here.

Size Impact on Diffusion

Diffusion of different species

Table 5.2 A Tabulation of Diffusion Data

Diffusing Species	*Host Metal*	D_0 (m^2/s)	*Activation Energy* Q_d *kJ/mol*	*eV/atom*	*Calculated Values* T(°C)	D (m^2/s)
Fe	α-Fe (BCC)	2.8×10^{-4}	251	2.60	500	3.0×10^{-21}
					900	1.8×10^{-15}
Fe	γ-Fe (FCC)	5.0×10^{-5}	284	2.94	900	1.1×10^{-17}
					1100	7.8×10^{-16}
C	α-Fe	6.2×10^{-7}	80	0.83	500	2.4×10^{-12}
					900	1.7×10^{-10}
C	γ-Fe	2.3×10^{-5}	148	1.53	900	5.9×10^{-12}
					1100	5.3×10^{-11}
Cu	Cu	7.8×10^{-5}	211	2.19	500	4.2×10^{-19}
Zn	Cu	2.4×10^{-5}	189	1.96	500	4.0×10^{-18}
Al	Al	2.3×10^{-4}	144	1.49	500	4.2×10^{-14}
Cu	Al	6.5×10^{-5}	136	1.41	500	4.1×10^{-14}
Mg	Al	1.2×10^{-4}	131	1.35	500	1.9×10^{-13}
Cu	Ni	2.7×10^{-5}	256	2.65	500	1.3×10^{-22}

Source: E. A. Brandes and G. B. Brook (Editors), *Smithells Metals Reference Book*, 7th edition, Butterworth-Heinemann, Oxford, 1992.

Smaller atoms diffuse faster

Important

- **Temperature - diffusion rate increases with increasing temperature (WHY ?)**
- **Diffusion mechanism – interstitials diffuse faster (WHY ?)**
- **Diffusing and host species - Do, Qd is different for every solute - solvent pair**
- **Microstructure - grain boundaries and dislocation cores provide faster pathways for diffusing species, hence diffusion is faster in polycrystalline vs. single crystal materials. (WHY ?)**

SUMMARY:
STRUCTURE & DIFFUSION

Diffusion FASTER for...

- open crystal structures
- lower melting T materials
- materials w/secondary bonding
- smaller diffusing atoms
- cations WHY ?
- lower density materials

Diffusion SLOWER for...

- close-packed structures
- higher melting T materials
- materials w/covalent bonding
- larger diffusing atoms
- anions
- higher density materials