

Defects

CHAPTER 4:

IMPERFECTIONS IN SOLIDS

ISSUES TO ADDRESS...

- What types of defects arise in solids?
- Can the number and type of defects be varied and controlled?
- How do defects affect material properties?
- Are defects undesirable?



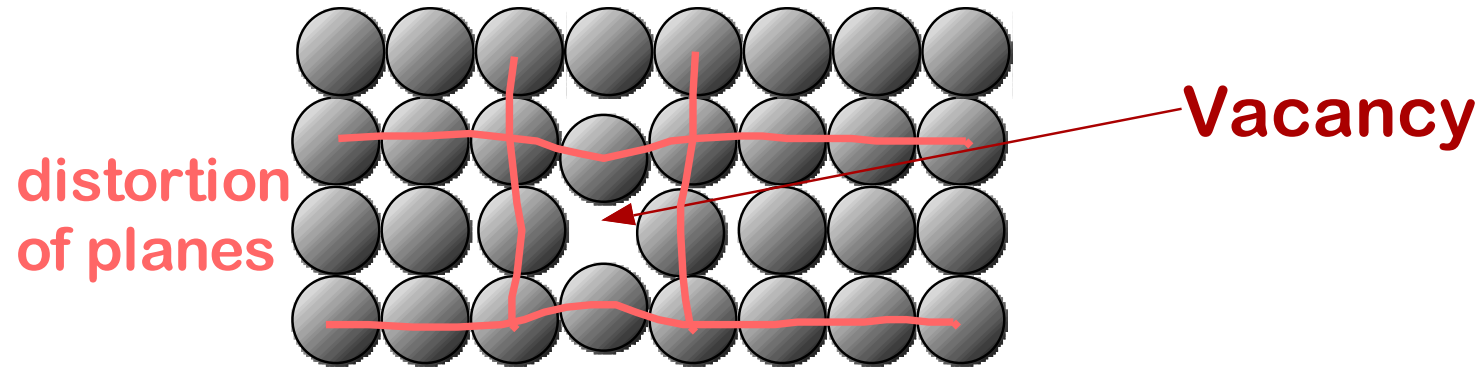
TYPES OF IMPERFECTIONS

• Vacancy atoms • Interstitial atoms • Substitutional atoms	Point defects
• Dislocations	Line defects
• Grain Boundaries	Area defects

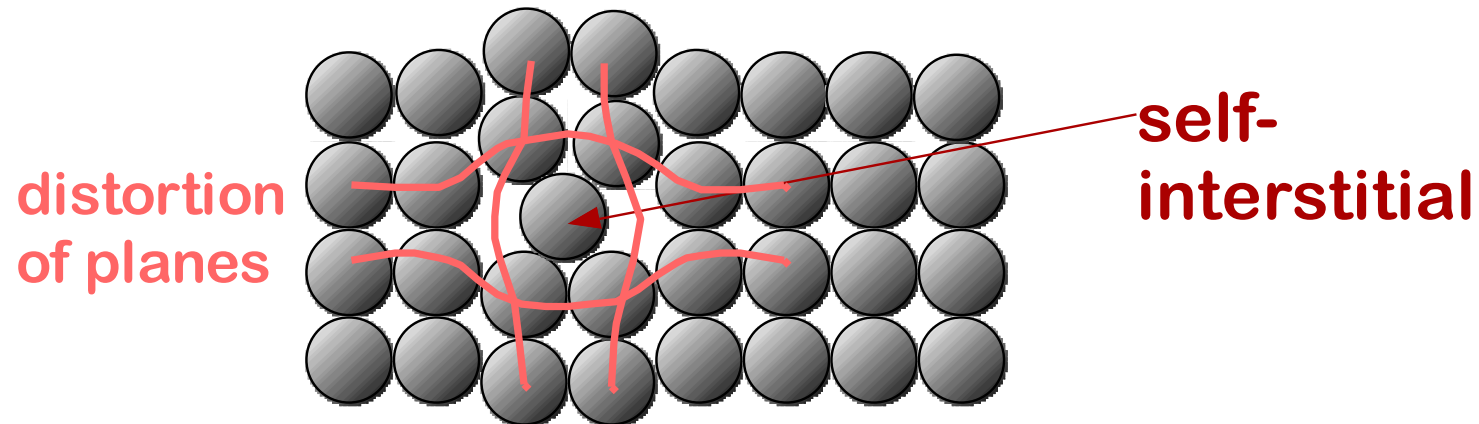


POINT DEFECTS

- **Vacancies:**
-vacant atomic sites in a structure.



- **Self-Interstitials:**
-"extra" atoms positioned between atomic sites.



EQUIL. CONCENTRATION: POINT DEFECTS

- Equilibrium concentration varies with temperature!

No. of defects N_D

No. of potential defect sites. N

Each lattice site is a potential vacancy site

Activation energy Q_D

Boltzmann's constant k

Temperature T

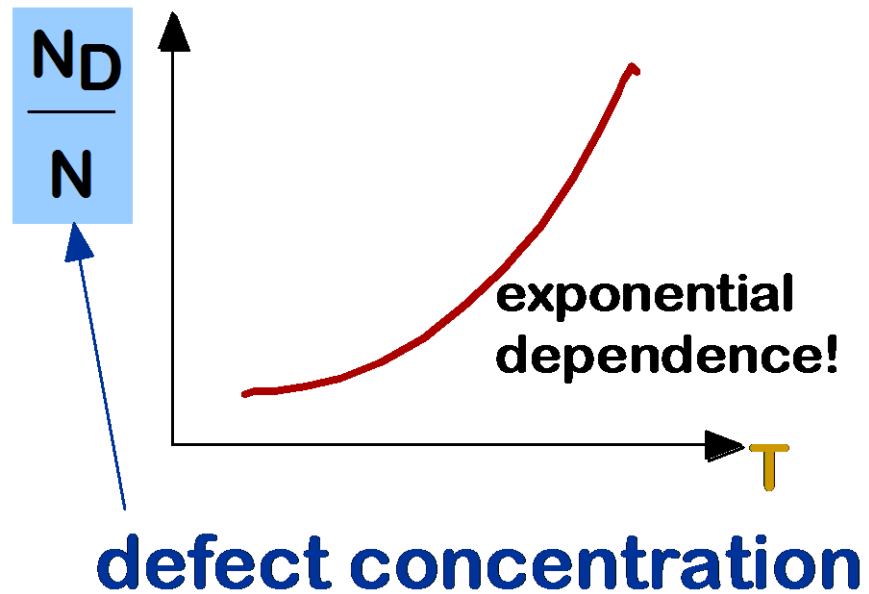
$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

(1.38 x 10⁻²³ J/atom K)
(8.62 x 10⁻⁵ eV/atom K)



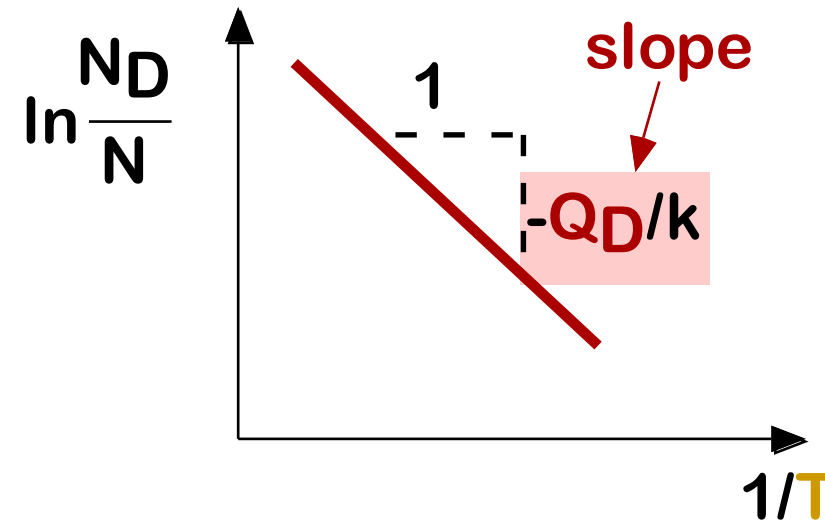
MEASURING ACTIVATION ENERGY

- We can get Q from an experiment.
- Measure this...



$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

- Replot it...



ESTIMATING VACANCY CONC.

- Find the equil. # of vacancies in 1m^3 of Cu at 1000C .
- Given:

$$\rho = 8.4 \text{ g/cm}^3 \quad A_{\text{Cu}} = 63.5\text{g/mol}$$

$$Q_V = 0.9\text{eV/atom} \quad N_A = 6.02 \times 10^{23} \text{ atoms/mole}$$

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right) = 2.7 \cdot 10^{-4}$$

Annotations for the equation above:

- Q_D is labeled 0.9eV/atom (red arrow)
- kT is labeled 1273K (yellow arrow)
- k is labeled $8.62 \times 10^{-5} \text{ eV/atom-K}$ (green arrow)

For 1m^3 , $N = \rho \times \frac{N_A}{A_{\text{Cu}}} \times 1\text{m}^3 = 8.0 \times 10^{28} \text{ sites}$

- Answer:

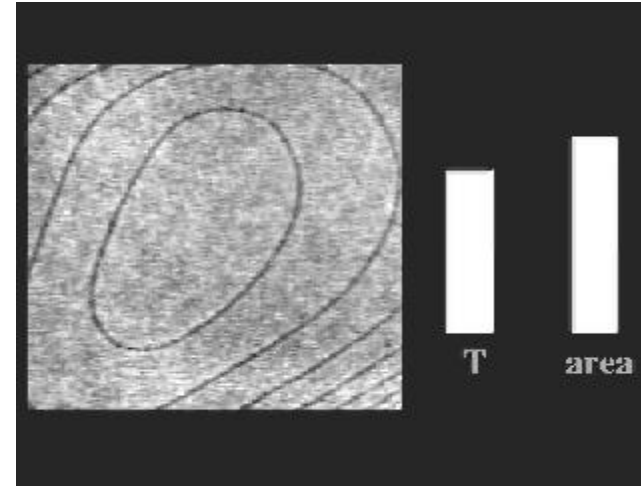
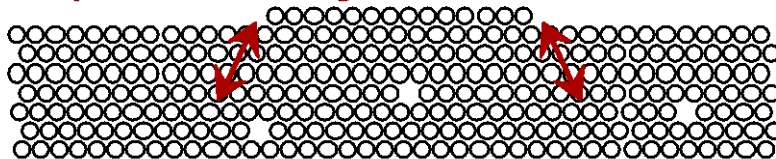
$$N_D = 2.7 \cdot 10^{-4} \cdot 8.0 \times 10^{28} \text{ sites} = 2.2 \times 10^{25} \text{ vacancies}$$



OBSERVING EQUIL. VACANCY CONC.

- Low energy electron microscope view of a (110) surface of NiAl.
- Increasing T causes surface island of atoms to grow.
- Why? The equil. vacancy conc. increases via atom motion from the crystal to the surface, where they join the island.

Island grows/shrinks to maintain equil. vacancy conc. in the bulk.

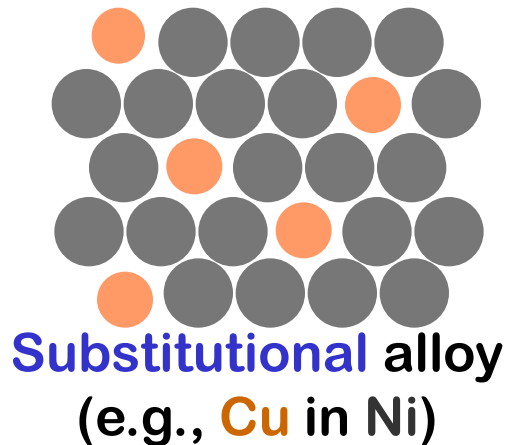


Reprinted with permission from [Nature](#) (K.F. McCarty, J.A. Nobel, and N.C. Bartelt, "Vacancies in Solids and the Stability of Surface Morphology", *Nature*, Vol. 412, pp. 622-625 (2001). Image is $5.75\ \mu\text{m}$ by $5.75\ \mu\text{m}$.) Copyright (2001) Macmillan Publishers, Ltd.

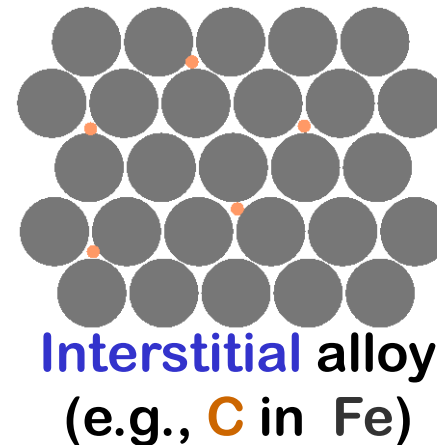
POINT DEFECTS IN ALLOYS

Two outcomes if impurity (B) added to host (A):

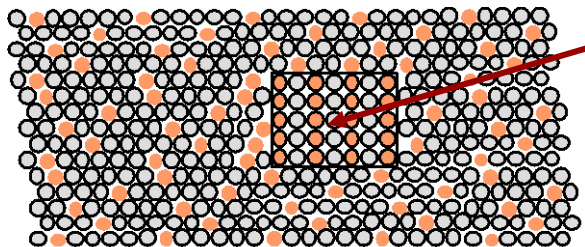
- **Solid solution** of **B** in A (i.e., random dist. of point defects)



OR



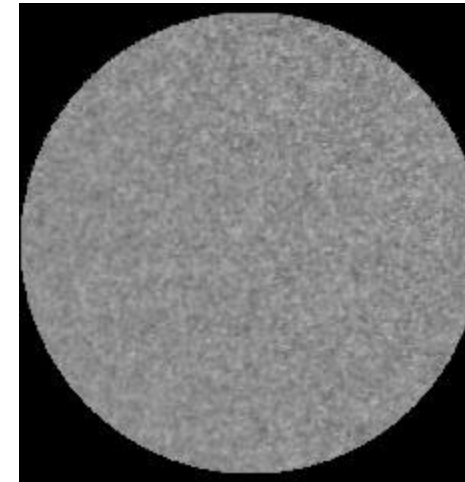
- Solid solution of **B** in A plus particles of a new phase (usually for a larger amount of B)



Second phase particle
--different **composition**
--often different structure.

ALLOYING A SURFACE

- Low energy electron microscope view of a (111) surface of Cu.
- Sn islands move along the surface and "alloy" the Cu with Sn atoms, to make "bronze".
- The islands continually move into "unalloyed" regions and leave tiny bronze particles in their wake.
- Eventually, the islands disappear.



Reprinted with permission from: A.K. Schmid, N.C. Bartelt, and R.Q. Hwang, "Alloying at Surfaces by the Migration of Reactive Two-Dimensional Islands", Science, Vol. 290, No. 5496, pp. 1561-64 (2000). Field of view is 1.5 μm and the temperature is 290K.



COMPOSITION

Definition: Amount of impurity (B) and host (A)
in the **system**.

Two descriptions:

- Weight %

$$C_B = \frac{\text{mass of B}}{\text{total mass}} \times 100$$

- Atom %

$$C'_B = \frac{\# \text{ atoms of B}}{\text{total \# atoms}} \times 100$$

- Conversion between wt % and at% in an A-B alloy:

$$C_B = \frac{C'_B A_B}{C'_A A_A + C'_B A_B} \times 100$$

$$C'_B = \frac{C_B / A_B}{C_A / A_A + C_B / A_B}$$

- Basis for conversion:

$$\text{mass of B} = \text{moles of B} \times A_B$$

$$\text{mass of A} = \text{moles of A} \times A_A$$

atomic weight of B

atomic weight of A



LINE DEFECTS

Dislocations:

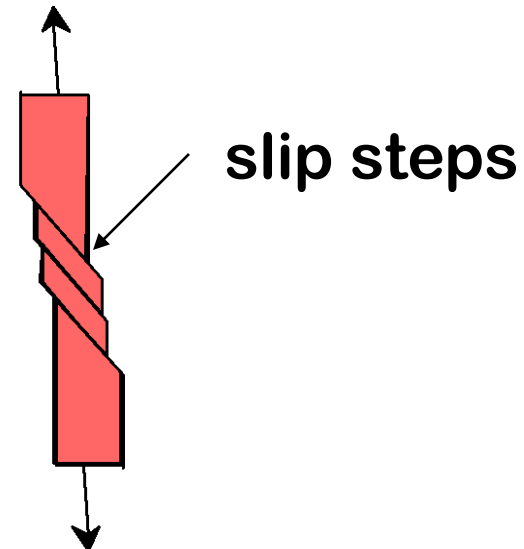
- are line defects,
- cause slip between crystal plane when they move,
- produce permanent (plastic) deformation.

Schematic of a Zinc (HCP):

- before deformation

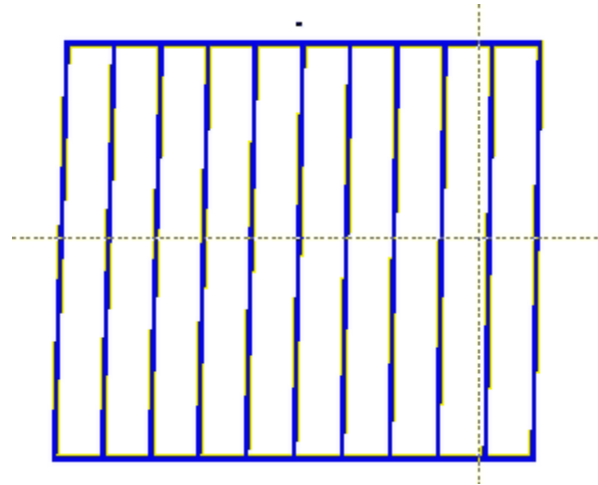


- after tensile elongation



INCREMENTAL SLIP

- Dislocations slip planes *incrementally*...
- The dislocation line (the moving red dot)...
...separates slipped material on the left
from unslipped material on the right.



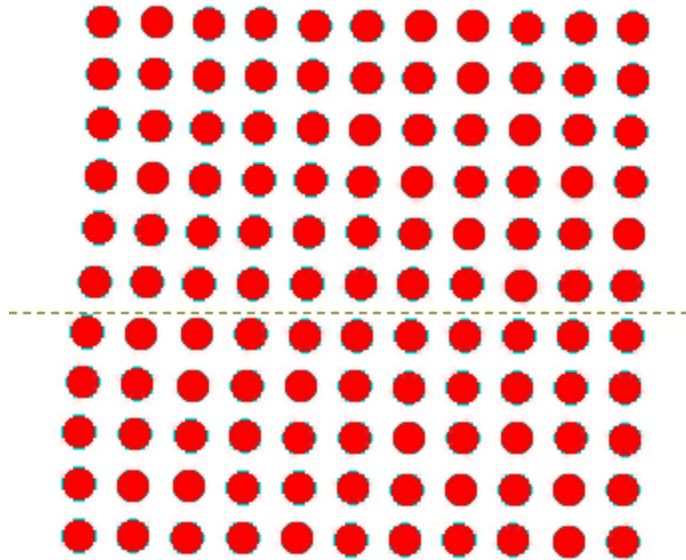
Simulation of dislocation motion from left to right as a crystal is sheared.

(Courtesy P.M. Anderson)



BOND BREAKING AND REMAKING

- Dislocation motion requires the successive bumping of a half plane of atoms (from left to right here).
- Bonds across the slipping planes are broken and remade in succession.



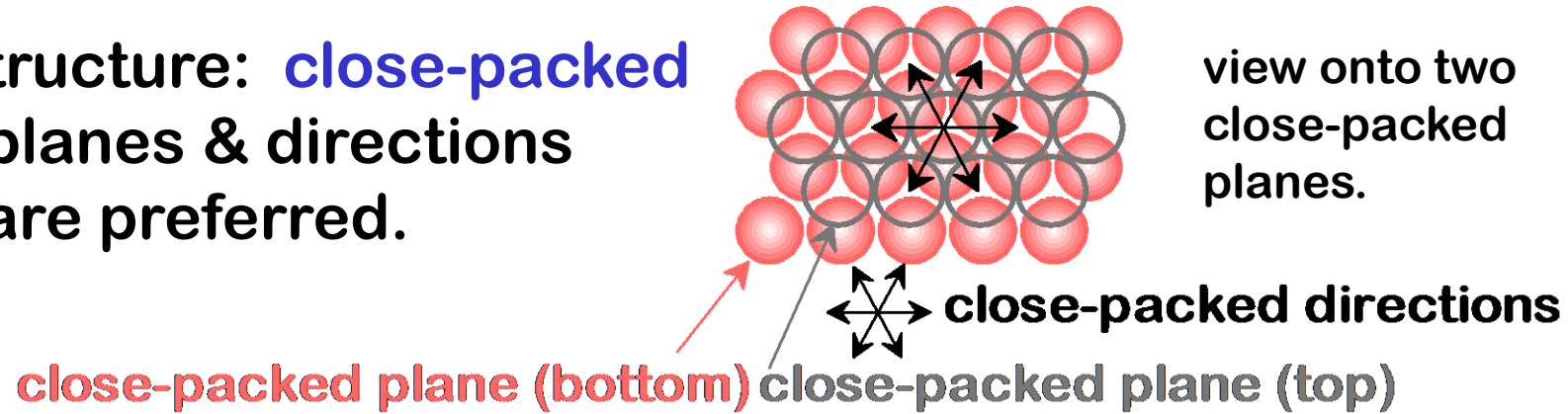
Atomic view of edge dislocation motion from left to right as a crystal is sheared.

(Courtesy P.M. Anderson)



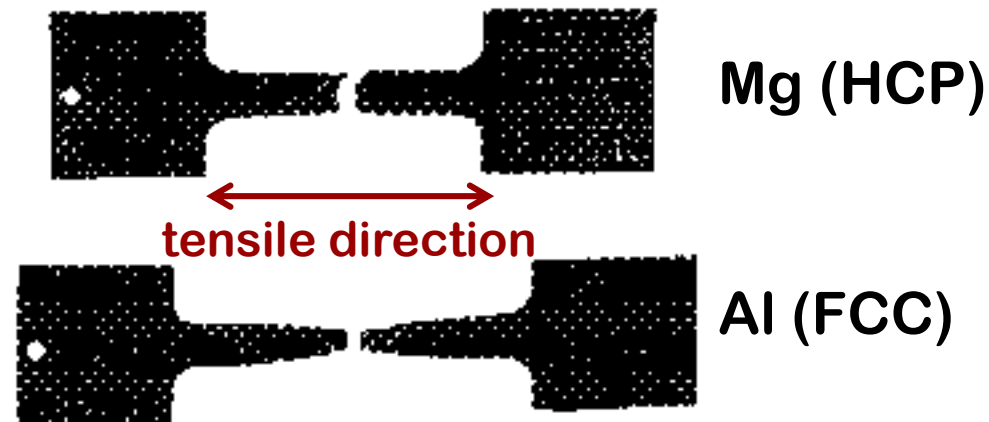
DISLOCATIONS & CRYSTAL STRUCTURE

- Structure: **close-packed** planes & directions are preferred.



- Comparison among crystal structures:
FCC: many close-packed planes/directions;
HCP: only one plane, 3 directions;
BCC: none

- Results of tensile testing.

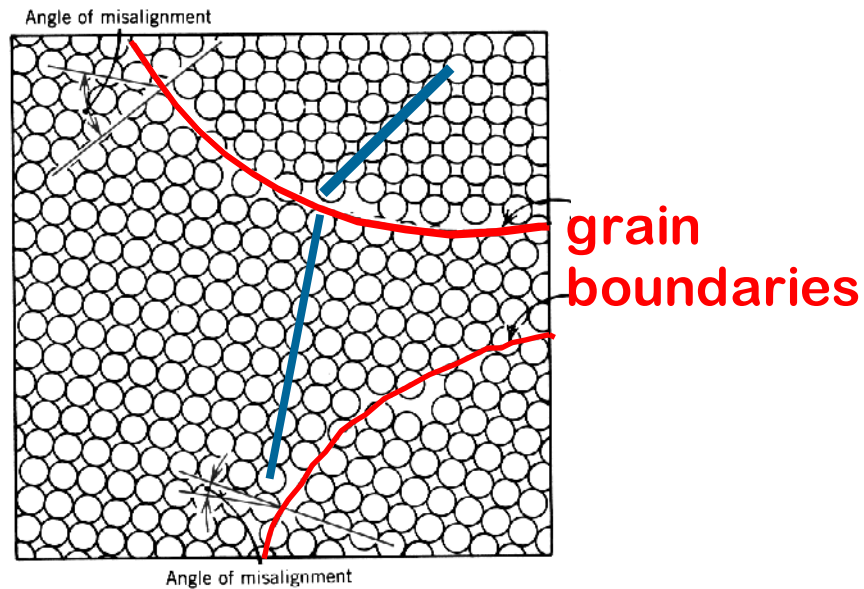


AREA DEFECTS: GRAIN BOUNDARIES

Grain boundaries:

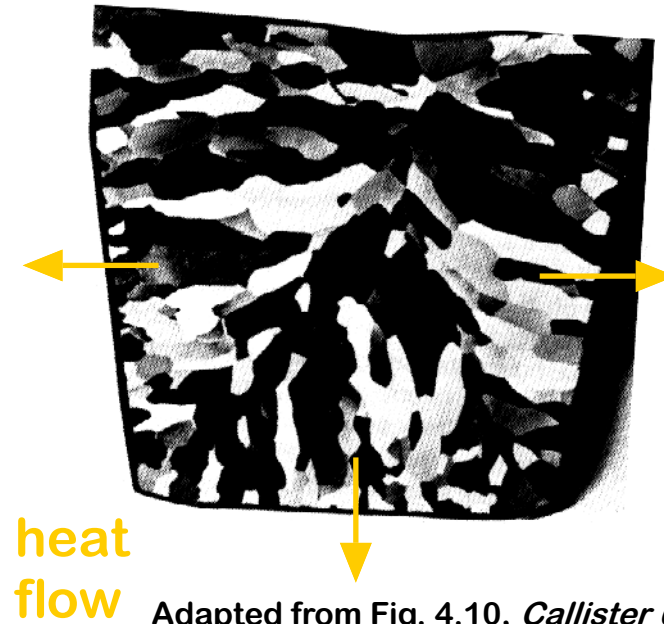
- are boundaries between crystals.
- are produced by the solidification process, for example.
- have a change in crystal orientation across them.
- impede dislocation motion.

Schematic



Adapted from Fig. 4.7, *Callister 6e*.

Metal Ingot
← ~ 8cm →



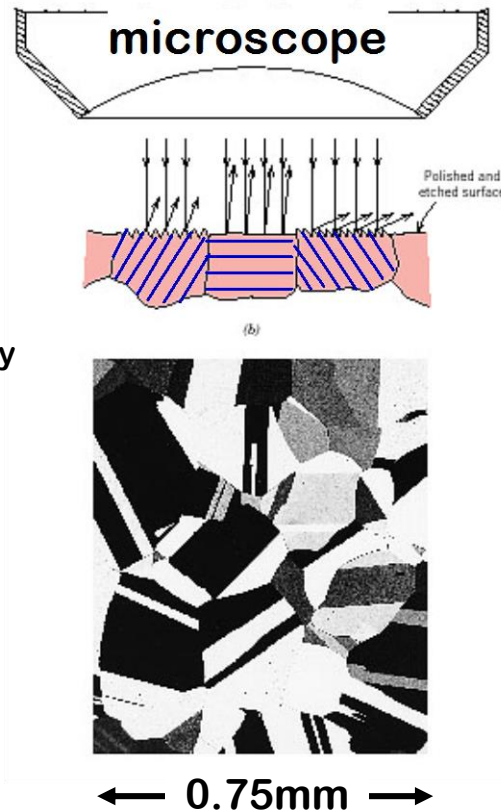
Adapted from Fig. 4.10, *Callister 6e*. (Fig. 4.10 is from *Metals Handbook*, Vol. 9, 9th edition, *Metallography and Microstructures*, Am. Society for Metals, Metals Park, OH, 1985.)



OPTICAL MICROSCOPY (1)

- Useful up to 2000X magnification.
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation.

Adapted from Fig. 4.11(b) and (c),
Callister 6e. (Fig. 4.11(c) is courtesy
of J.E. Burke, General Electric Co.



close-packed planes

micrograph of
Brass (Cu and Zn)

OPTICAL MICROSCOPY (2)

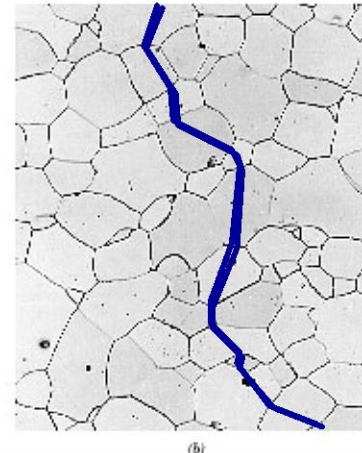
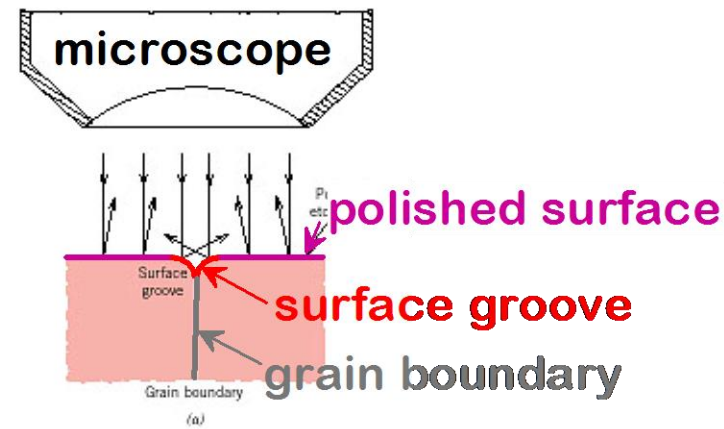
Grain boundaries...

- are imperfections,
- are more susceptible to etching,
- may be revealed as dark lines,
- change direction in a polycrystal.

ASTM grain
size number

$$N = 2^{n-1}$$

no. grains/in²
at 100x
magnification



Adapted from Fig. 4.12(a) and (b), *Callister 6e*. (Fig. 4.12(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)



SUMMARY

- **Point, Line, and Area** defects arise in solids.
- The number and type of defects can be varied and controlled (e.g., T controls vacancy conc.)
- Defects affect material properties (e.g., grain boundaries control crystal slip).
- Defects may be desirable or undesirable (e.g., dislocations may be good or bad, depending on whether plastic deformation is desirable or not.)



CHAPTER 5:

DIFFUSION IN SOLIDS

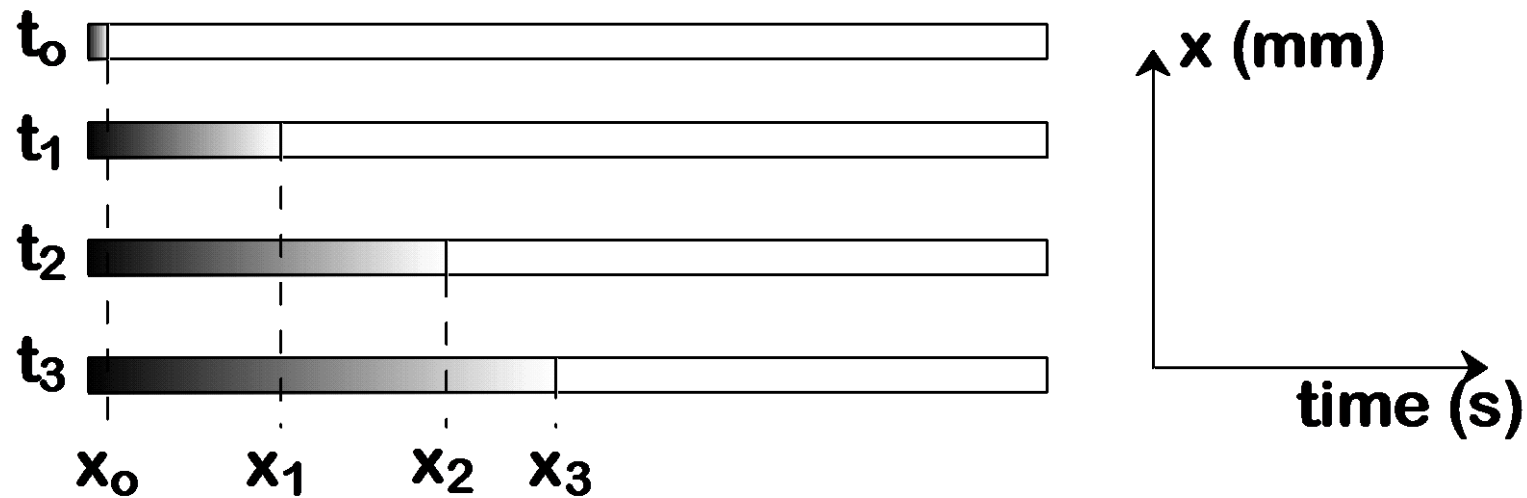
ISSUES TO ADDRESS...

- 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?



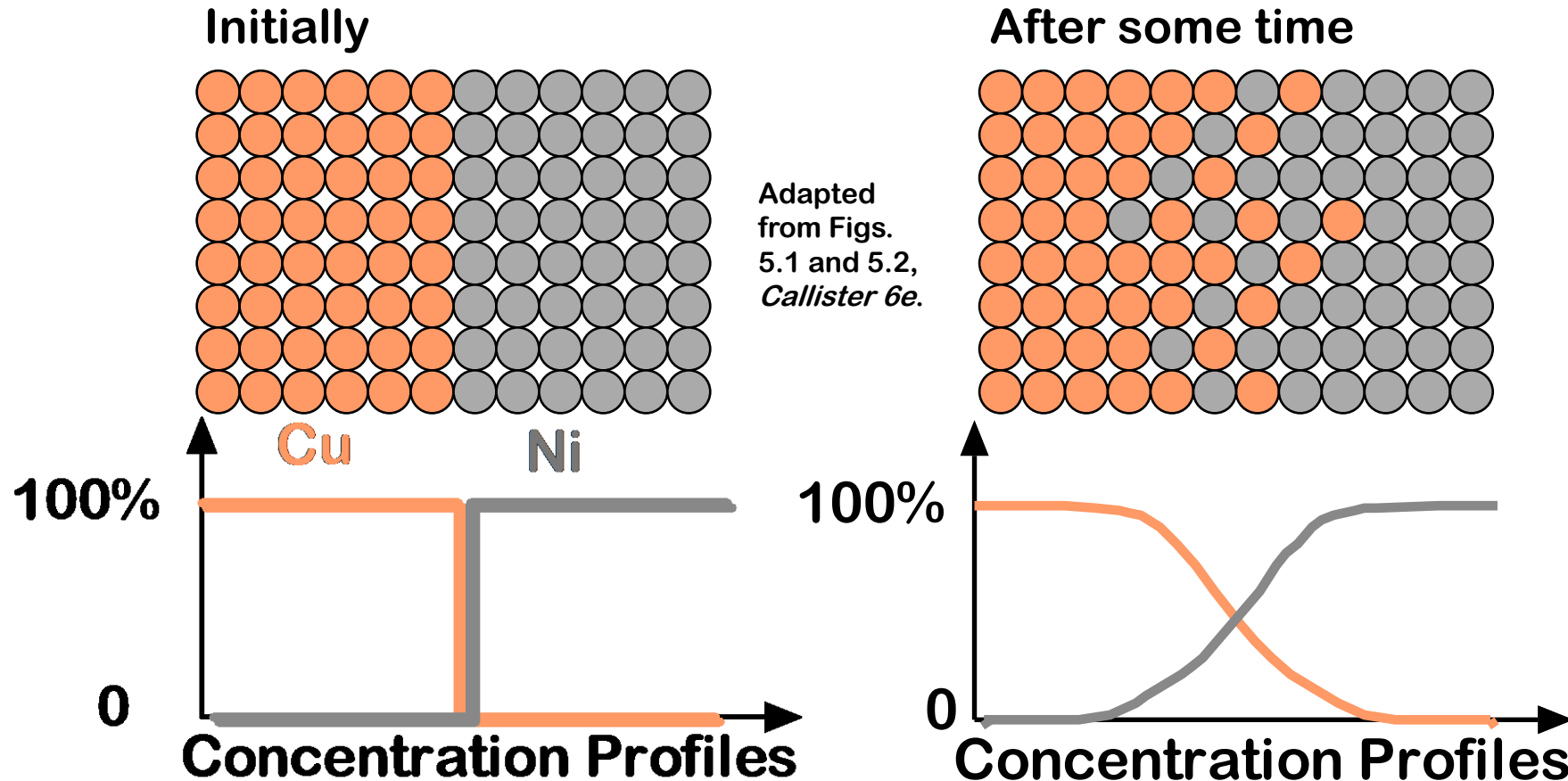
DIFFUSION DEMO

- 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.



DIFFUSION: THE PHENOMENA (1)

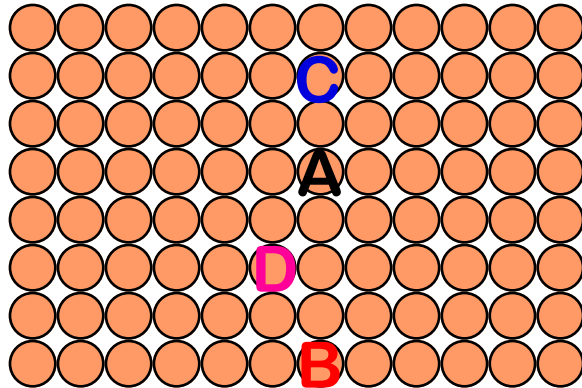
- **Interdiffusion:** In an alloy, atoms tend to migrate from regions of large concentration.



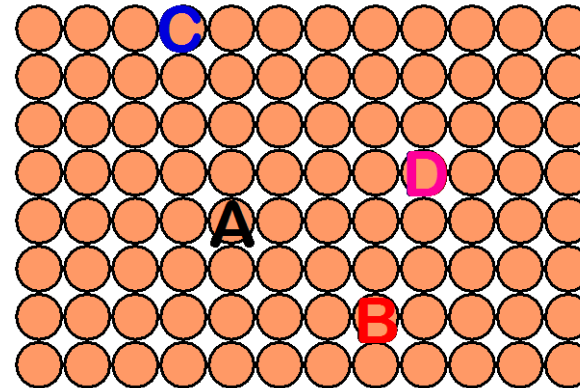
DIFFUSION: THE PHENOMENA (2)

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

Label some atoms



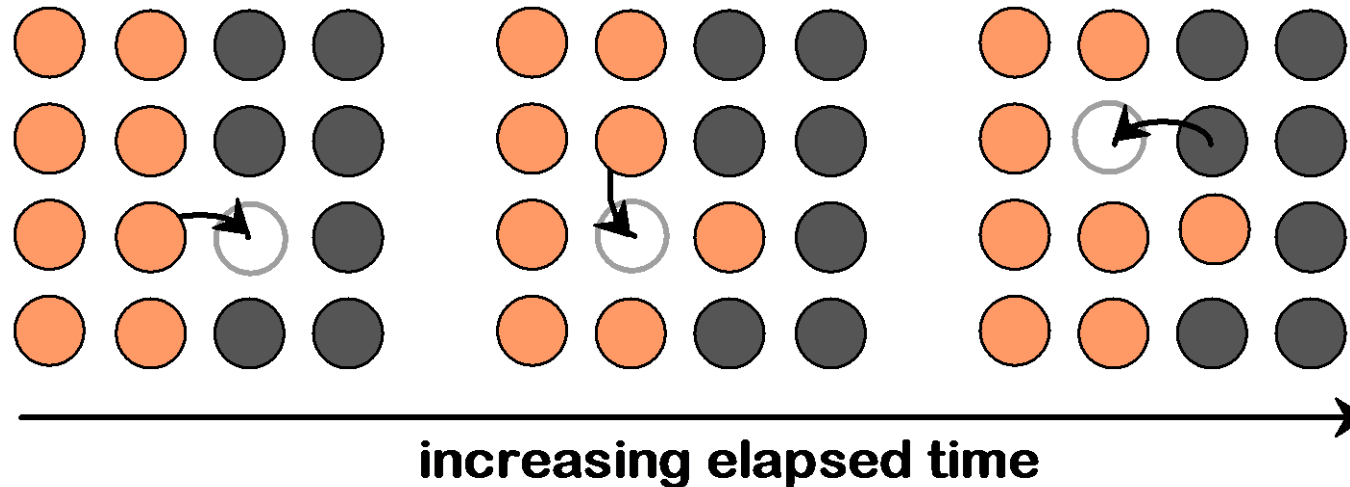
After some time



DIFFUSION MECHANISMS

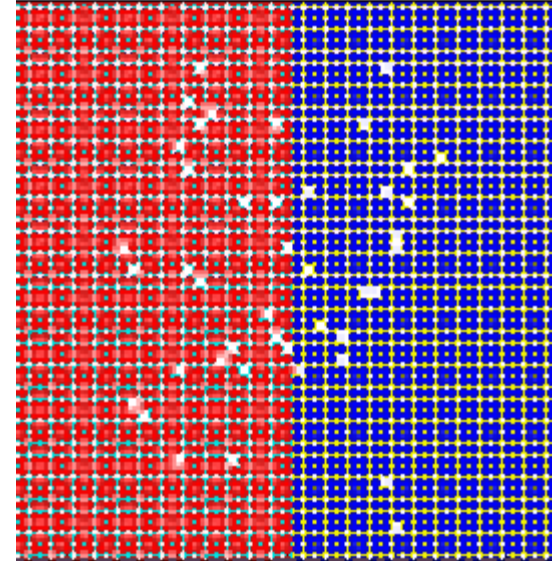
Substitutional Diffusion:

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



DIFFUSION SIMULATION

- Simulation of interdiffusion across an interface:
- Rate of substitutional diffusion depends on:
 - vacancy concentration
 - frequency of jumping.

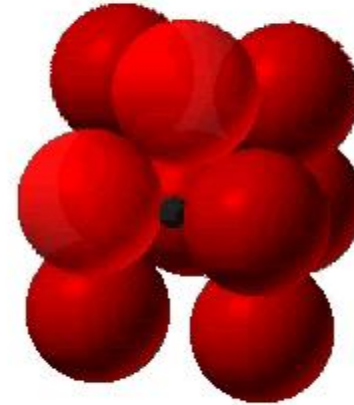


(Courtesy P.M. Anderson)



INTERSTITIAL SIMULATION

- Applies to interstitial impurities.
- More rapid than vacancy diffusion.
- Simulation:
 - shows the jumping of a smaller atom (gray) from one interstitial site to another in a BCC structure. The interstitial sites considered here are at midpoints along the unit cell edges.



(Courtesy P.M. Anderson)

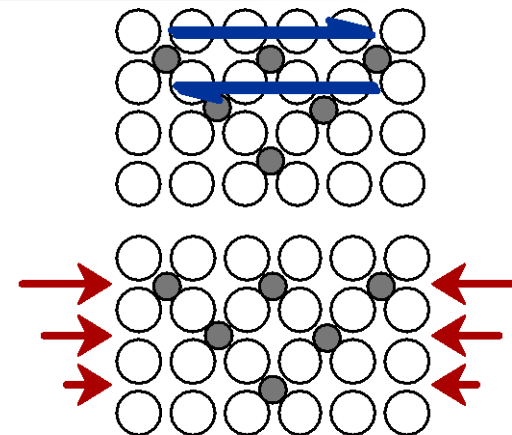


PROCESSING USING DIFFUSION (1)

- **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**.



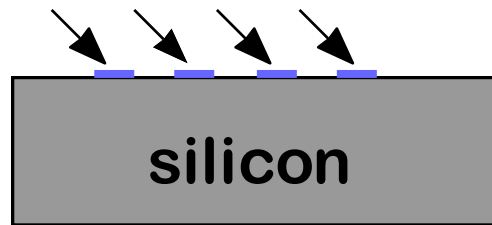
Fig. 5.0,
Callister 6e.
(Fig. 5.0 is
courtesy of
Surface
Division,
Midland-
Ross.)



PROCESSING USING DIFFUSION (2)

- **Doping** Silicon with P for n-type semiconductors:
- **Process:**

1. Deposit **P** rich layers on surface.



2. **Heat it.**

3. Result: Doped semiconductor regions.

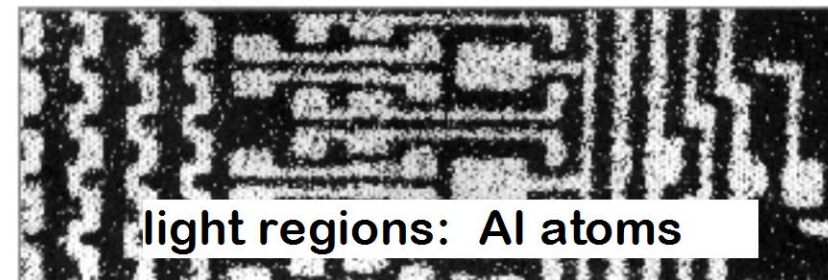
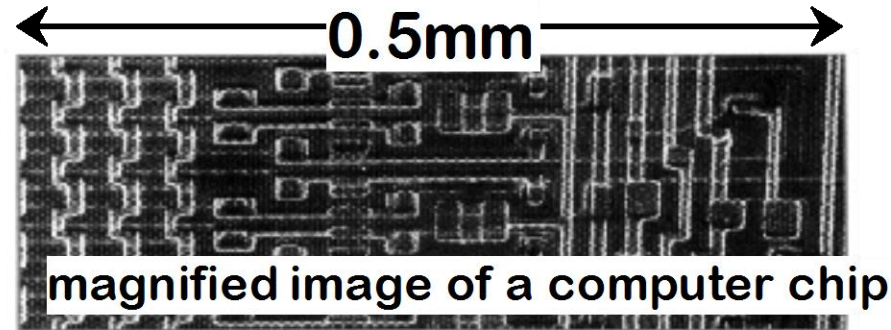
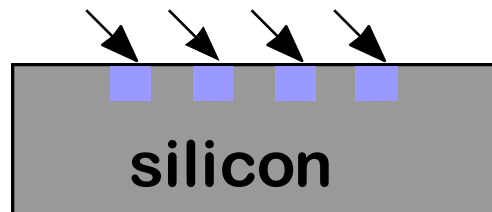


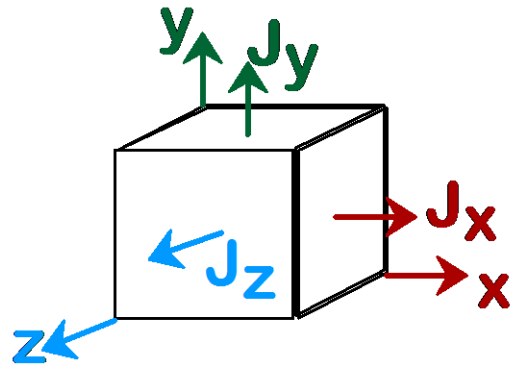
Fig. 18.0,
Callister 6e.

MODELING DIFFUSION: FLUX

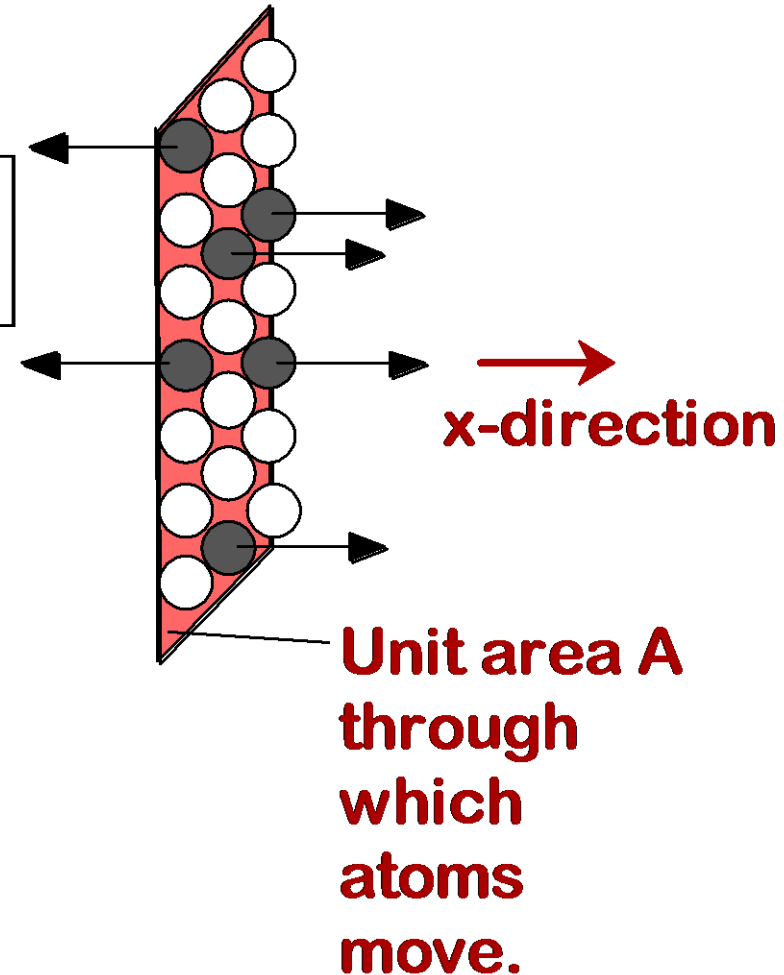
- Flux:

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

- Directional Quantity

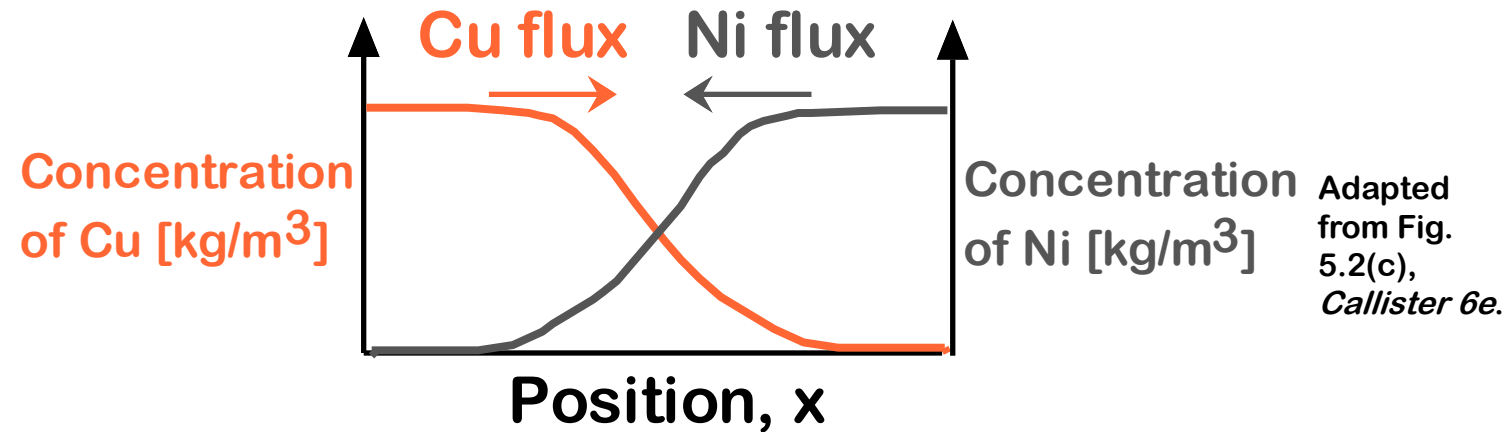


- Flux can be measured for:
 - vacancies
 - host (A) atoms
 - impurity (B) atoms



CONCENTRATION PROFILES & FLUX

- **Concentration Profile, $C(x)$: [kg/m³]**



- **Fick's First Law:**

flux in x-dir.
[kg/m²-s] $\rightarrow J_x = -D \frac{dC}{dx}$

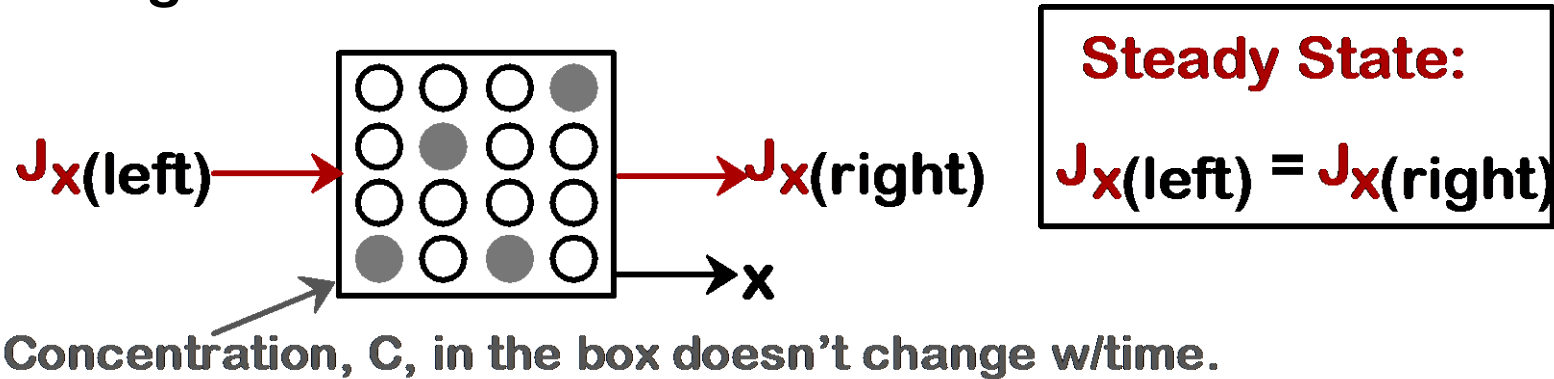
Diffusion coefficient [m²/s] $\rightarrow D$

concentration gradient [kg/m⁴] $\rightarrow \frac{dC}{dx}$

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

STEADY STATE DIFFUSION

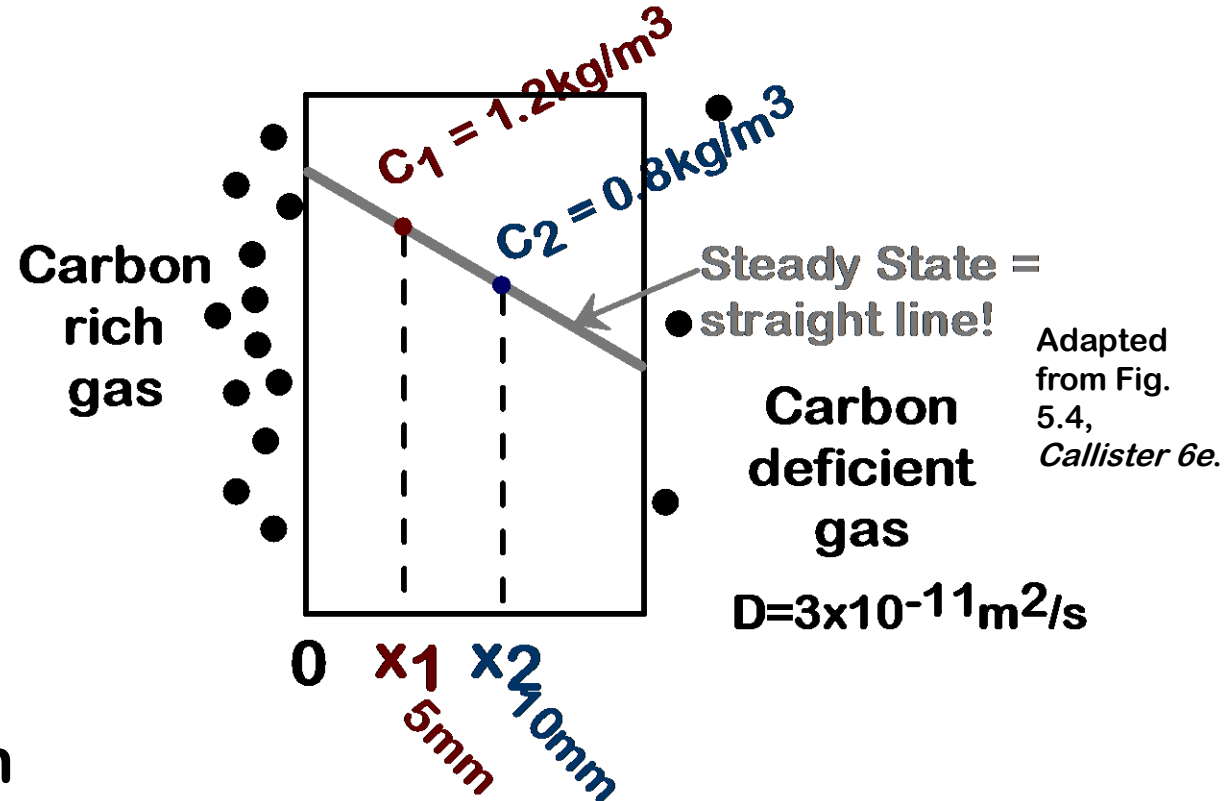
- **Steady State**: the concentration profile doesn't change with time.



- Apply Fick's First Law: $J_x = -D \frac{dC}{dx}$
- If $J_x(\text{left}) = J_x(\text{right})$, then $\left(\frac{dC}{dx} \right)_{\text{left}} = \left(\frac{dC}{dx} \right)_{\text{right}}$
- Result: the slope, dC/dx , must be constant (i.e., slope doesn't vary with position)!

EX: STEADY STATE DIFFUSION

- Steel plate at 700C with geometry shown:

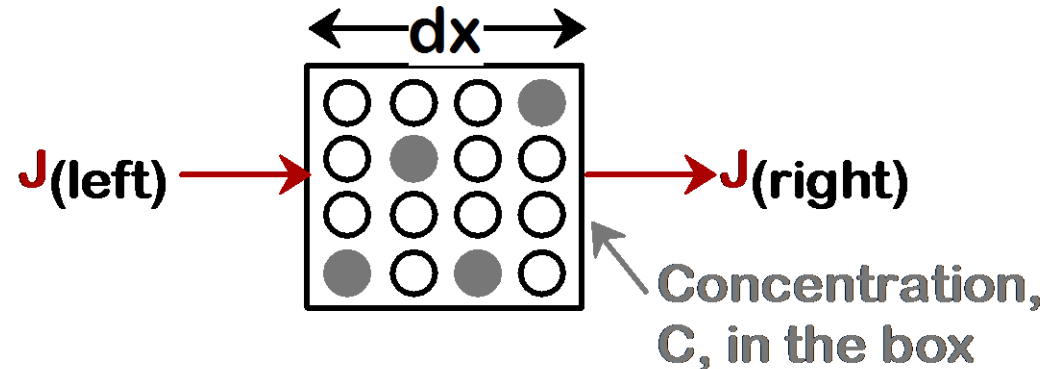


- Q: How much carbon transfers from the rich to the deficient side?

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

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:

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

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

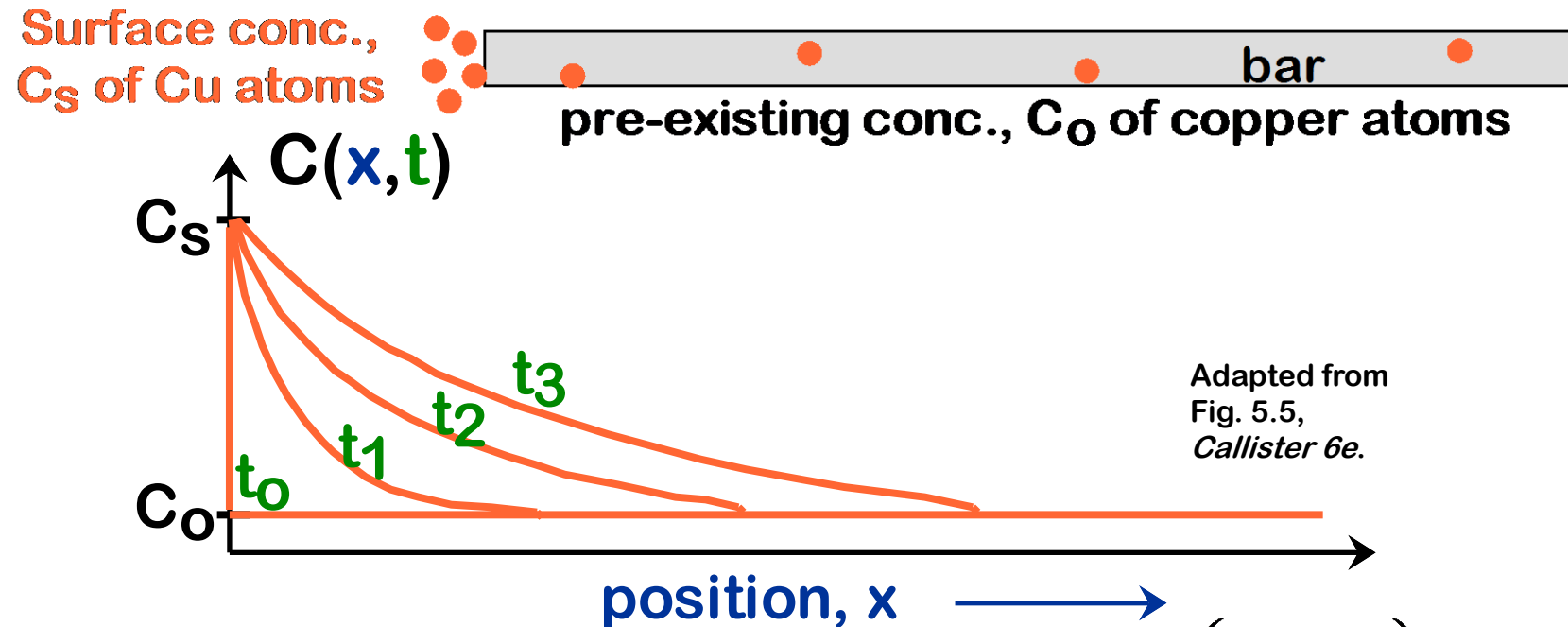
equate

- Governing Eqn.:

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

EX: NON STEADY STATE DIFFUSION

- Copper diffuses into a bar of aluminum.



- General solution:
$$\frac{C(x, t) - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$
- "error function"

Values calibrated in Table 5.1, *Callister 6e*.

PROCESSING QUESTION

- 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_0 and C_s .

- Result: Dt should be held constant.

$$\frac{C(x, t) - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{\sqrt{2Dt}}\right) \rightarrow (Dt)_{500^\circ\text{C}} = (Dt)_{600^\circ\text{C}}$$

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

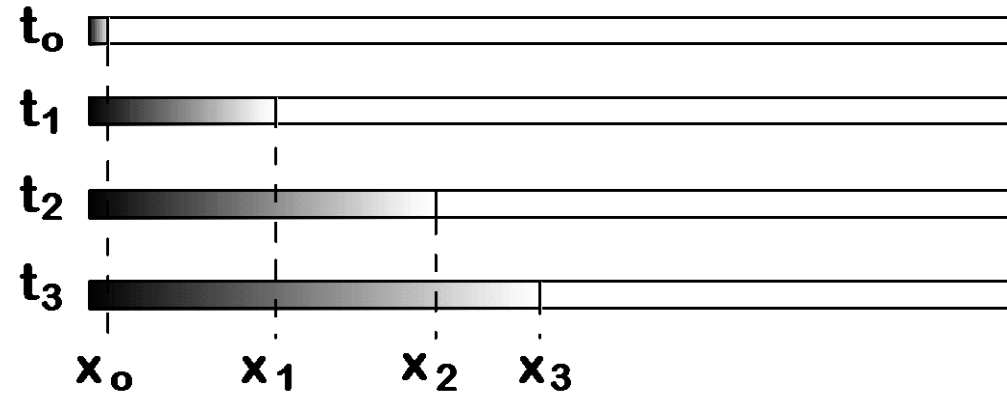
Annotations: $5.3 \times 10^{-13} \text{m}^2/\text{s}$ points to $(Dt)_{600}$; 10hrs points to $(Dt)_{600}$; $4.8 \times 10^{-14} \text{m}^2/\text{s}$ points to D_{500} .

Note: values of D are provided here.



DIFFUSION DEMO: ANALYSIS

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



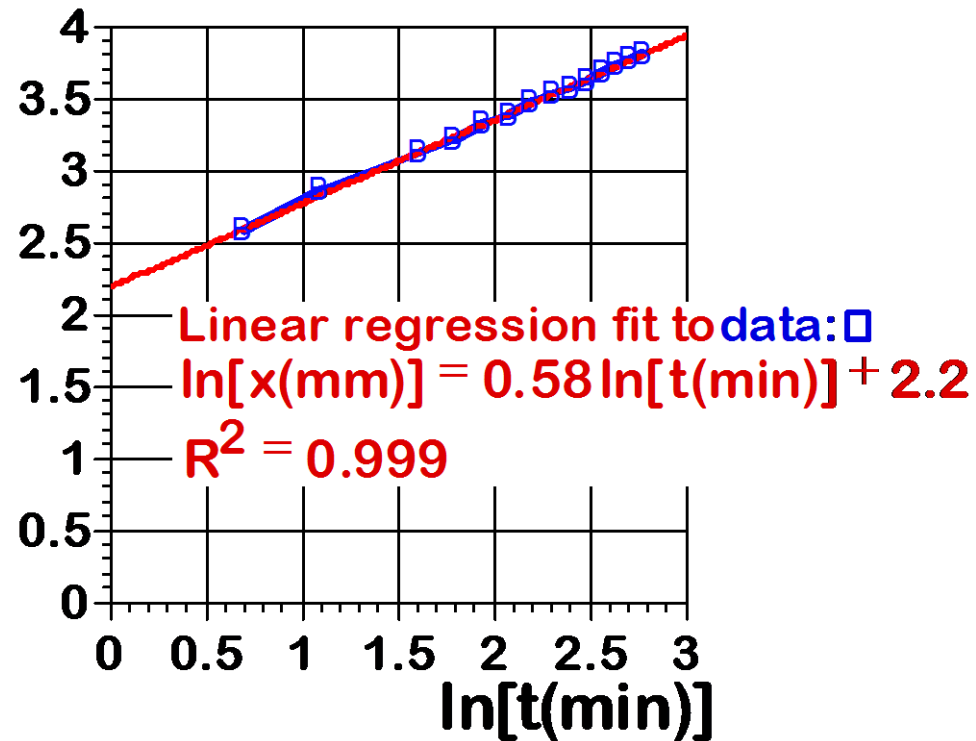
$$\frac{C(x_i, t_i) - C_0}{C_S - C_0} = 1 - \operatorname{erf} \left(\frac{x_i}{2\sqrt{Dt_i}} \right) = (\text{constant here})$$

- 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!



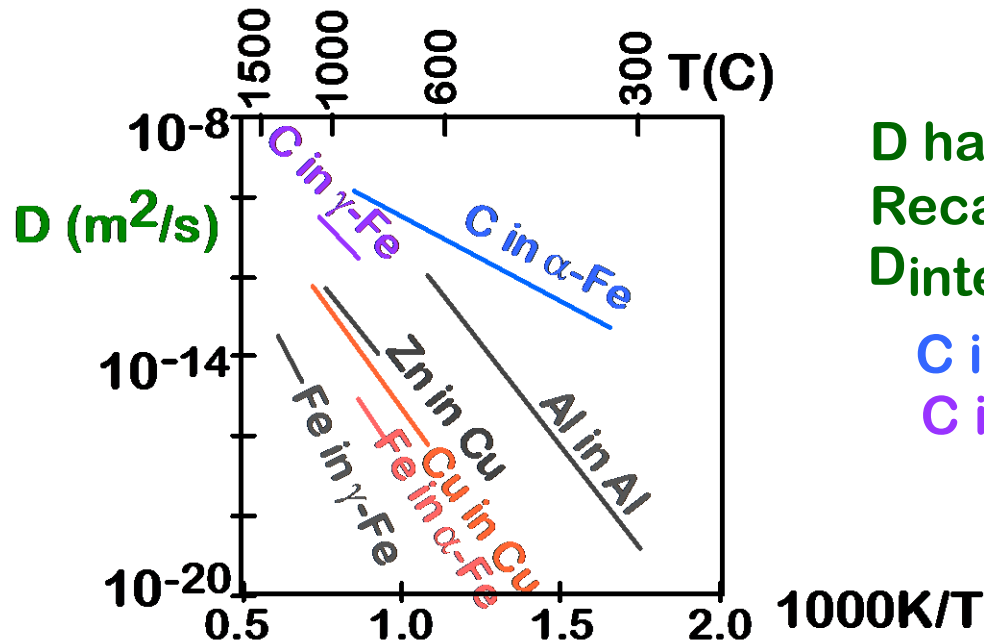
DIFFUSION AND TEMPERATURE

- Diffusivity increases with T.

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

D_0 : pre-exponential [m^2/s] (see Table 5.2, *Callister 6e*)
 Q_d : activation energy [J/mol], [eV/mol] (see Table 5.2, *Callister 6e*)
 R : gas constant [8.31 J/mol-K]

- Experimental Data:



D has exp. dependence on T
 Recall: Vacancy does also!
 $D_{\text{interstitial}} \gg D_{\text{substitutional}}$

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

Adapted from Fig. 5.7, *Callister 6e*. (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.)

