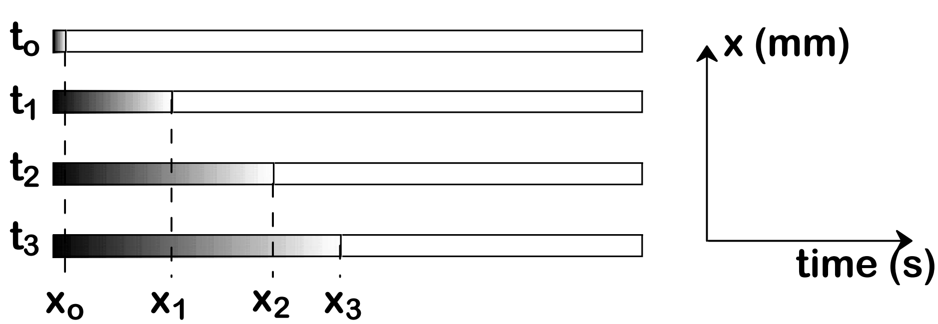
CHAPTER 5: DIFFUSION IN SOLIDS

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

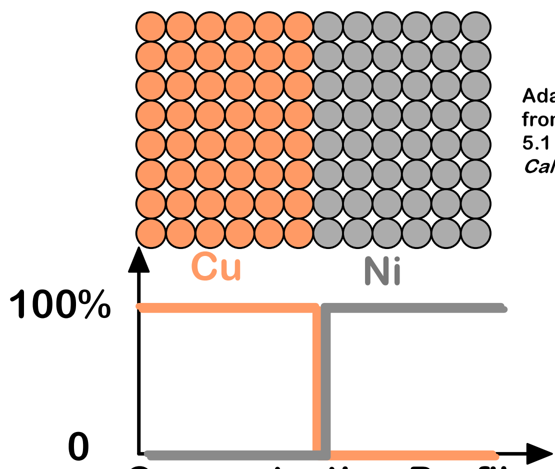
- Glass tube filled with water.
- At time t = 0, add some drops of ink to one end of the tube.
- Measure the diffusion distance, x, over some time.
- Compare the results with theory.



DIFFUSION: THE PHENOMENA (1)

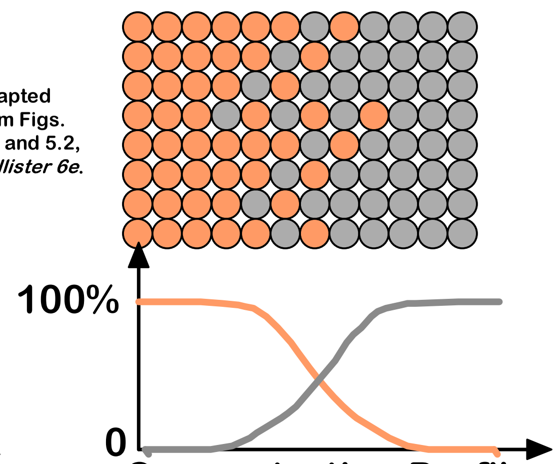
- **Interdiffusion**: In an alloy, atoms tend to migrate from regions of high concentration to regions of low concentration.

Initially



Adapted from Figs. 5.1 and 5.2, *Callister 6e.*

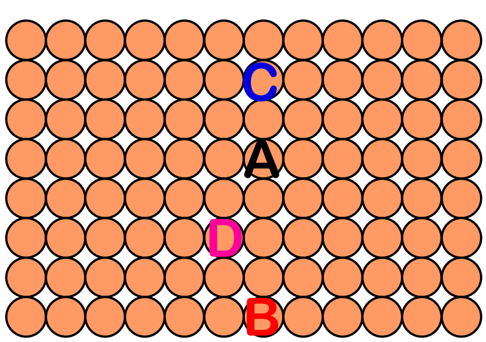
After some time



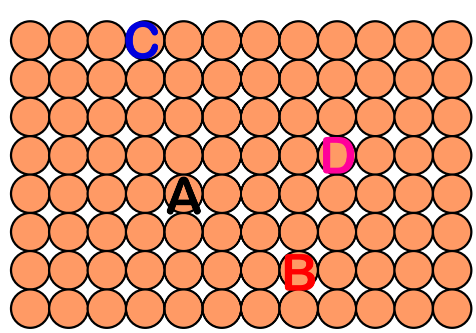
DIFFUSION: THE PHENOMENA (2)

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

Label some atoms



After some time



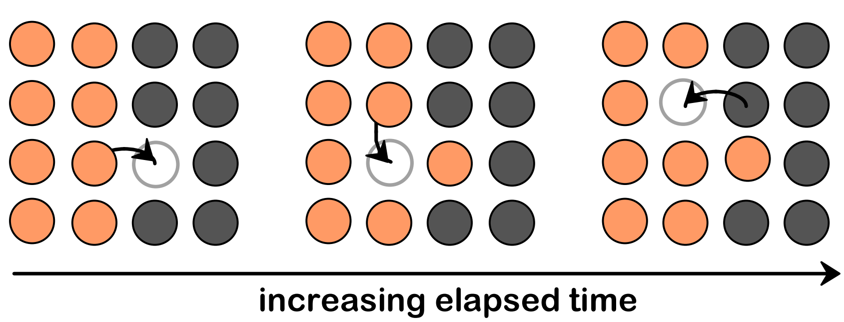
Diffusion: The Mechanism

- All atoms are constantly vibrating around their lattice positions (as long as temperature is above absolute zero).
- The atoms vibrate with a distribution of frequencies and amplitudes, i.e. there is a distribution of vibrational energies
- For one atom, the vibrational energy will vary over time
- As temperature increases the average vibrational energy increases

Diffusion is the movement of an atom from one lattice position to another. An atom can diffuse if (1) there is an adjacent space and (2) the atom has sufficient energy

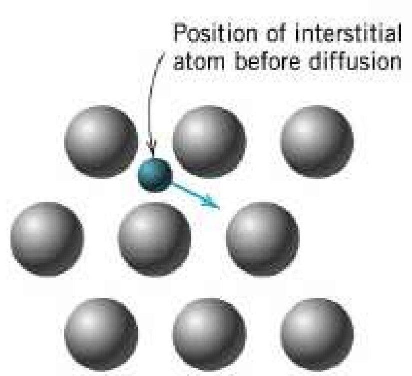
Substitutional Diffusion

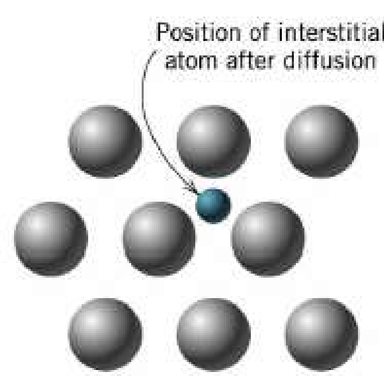
- **applies to substitutional impurities**
- **atoms exchange with vacancies**
- **rate depends on:**
  --number of vacancies
  --activation energy to exchange.



INTERSTITIAL DIFFUSION

- Applies to interstitial impurities.
- More rapid than vacancy diffusion.





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.

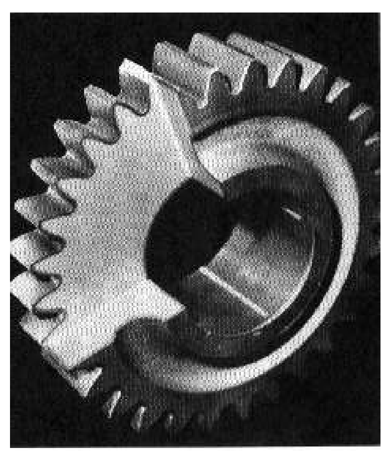
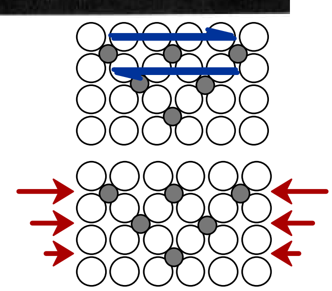


Fig. 5.0, *Callister 6e*. (Fig. 5.0 is courtesy of Surface Division, Midland-Ross.)

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

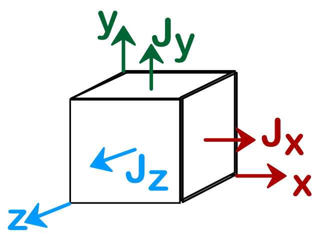


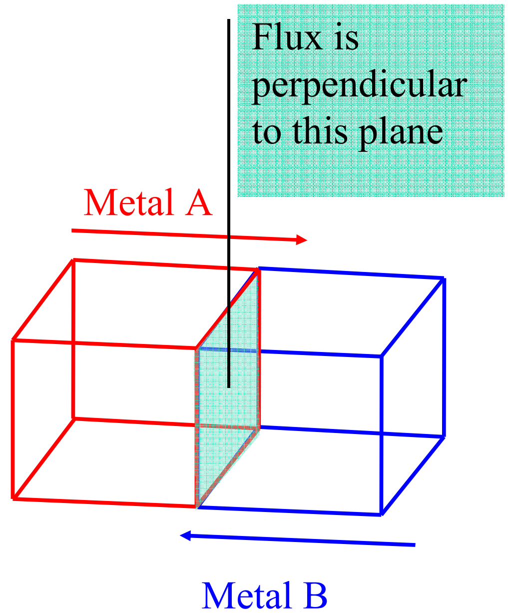
MODELING DIFFUSION: FLUX

- **Flux**:

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

- **Directional Quantity**

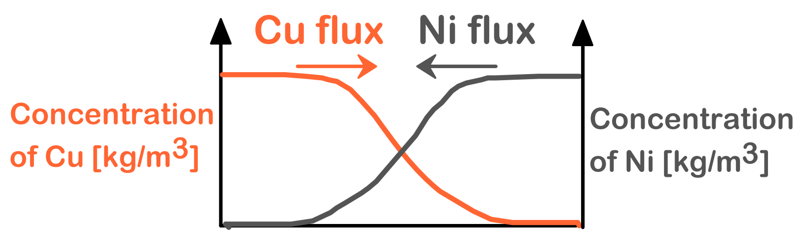




- **Flux can be measured for:**
  --vacancies
  --host (A) atoms
  --impurity (B) atoms

CONCENTRATION PROFILES & FLUX

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



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

- **Fick's First Law:**

flux in x-dir. [kg/m²-s]
Diffusion coefficient [m²/s]

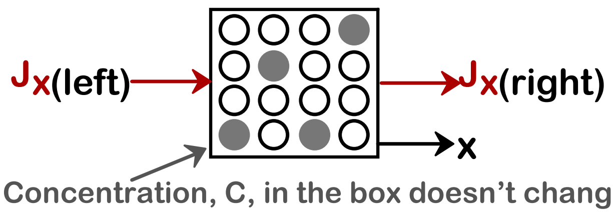
$$J_x = -D\frac{dC}{dx}$$

concentration gradient [kg/m⁴]

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

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

Diffusion Coefficient, D

- Also called diffusivity
- Units: m^2/s
- Depends on diffusing species and host
- Depends on temperature
- Higher diffusivity means a higher flux for the same concentration gradient

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

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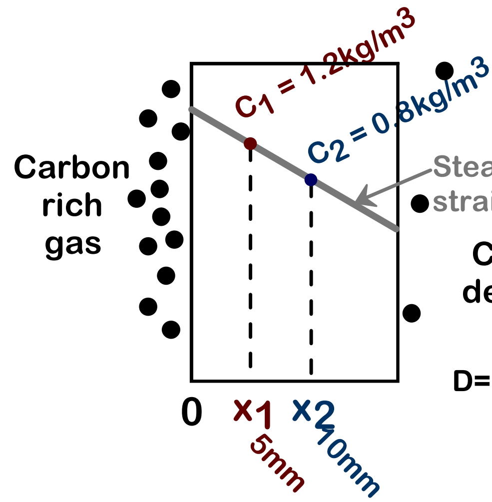
EX: STEADY STATE DIFFUSION

- Steel plate at 700°C with geometry shown:



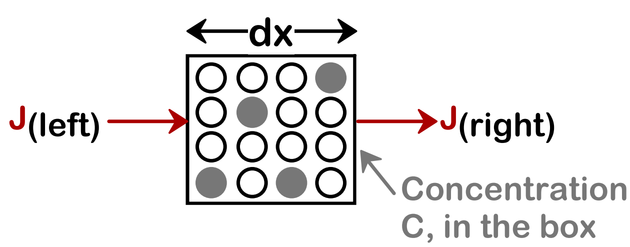
Adapted from Fig. 5.4, *Callister 6e.*

$D=3 \times 10^{-11} m^2/s$

- Q: What is the flux of carbon from the left to the right?

NON STEADY STATE DIFFUSION

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



- To conserve matter:

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

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

- Fick's First Law:

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

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

equate

- Governing Eqn.:

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

Fick's 2nd Law

Non-steady state diffusion

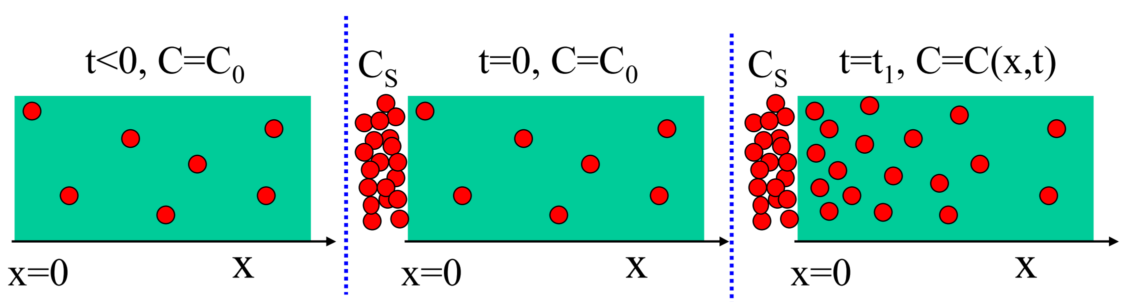
$$\boxed{\frac{dC}{dt} = D\frac{d^2C}{dx^2}}$$

Fick's 2nd Law

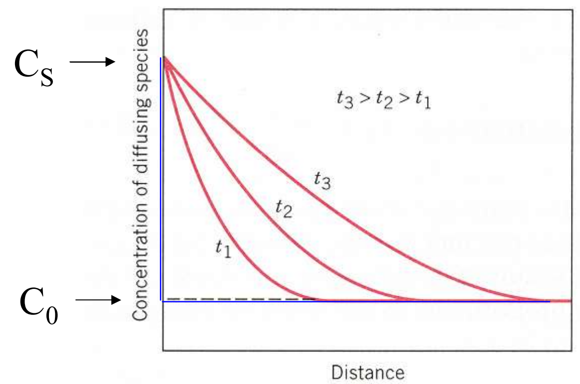
- In order to analyze non-steady state diffusion behavior we must solve this partial differential equation.
- The solution depends on the initial conditions and the boundary conditions.
- We will consider one type of non-steady state diffusion only.

Diffusion through a semi infinite solid with constant surface concentration

- We can use this approximation if $L > 10\sqrt{Dt}$
- Before diffusion begins the diffusing atoms are uniformly distributed in the solid at a concentration C_0.
- At t=0 the concentration at the surface of the solid is suddenly changed to C_S.



Diffusion through a semi infinite solid with constant surface concentration



Blue line is the concentration profile at t=0.

Solution to Fick's 2nd Law for this case:

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

Error Function Table

Table 5.1 Tabulation of Error Function Values

z	erf(z)	z	erf(z)	z	erf(z)
0	0	0.55	0.5633	1.3	0.9340
0.025	0.0282	0.60	0.6039	1.4	0.9523
0.05	0.0564	0.65	0.6420	1.5	0.9661
0.10	0.1125	0.70	0.6778	1.6	0.9763
0.15	0.1680	0.75	0.7112	1.7	0.9838
0.20	0.2227	0.80	0.7421	1.8	0.9891
0.25	0.2763	0.85	0.7707	1.9	0.9928
0.30	0.3286	0.90	0.7970	2.0	0.9953
0.35	0.3794	0.95	0.8209	2.2	0.9981
0.40	0.4284	1.0	0.8427	2.4	0.9993
0.45	0.4755	1.1	0.8802	2.6	0.9998
0.50	0.5205	1.2	0.9103	2.8	0.9999

Note: z is the independent variable, i.e. $Z = \frac{x}{2\sqrt{Dt}}$

and erf(z) is the dependent variable.

Example 1

Consider the impurity diffusion of gallium into a silicon wafer at 1100°C. Prior to commencement of diffusion the wafer was free of gallium. At time = 0 the surface concentration is changed to 10^{24} atoms/m^3. Find the depth below the surface at which the concentration will be 10^{22} atoms/m^3 after 3 hours.

Given: $D=7.0 \times 10^{-17}$ m^2/s

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Example 2

Consider the gas carburizing of steel at 927ºC. The diffusion coefficient of carbon in steel at this temperature is 1.28 x 10-11 m^2/s. The carbon content at the surface is 0.90% and the initial carbon content is 0.20%. Calculate the carbon content 0.50 mm below the surface after 5 hours of carburizing time.

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Example 3

Consider the surface treatment of steel with C at 950°C. The initial concentration of C in the steel is 0.25 wt% and the surface concentration during treatment is 1.2 wt%. How long will it take to reach 0.8 wt% C at a position of 0.5 mm below the surface?

Given: $D=1.6 \times 10^{-11}$ m^2/s

DIFFUSION AND TEMPERATURE

- Diffusivity increases with T.

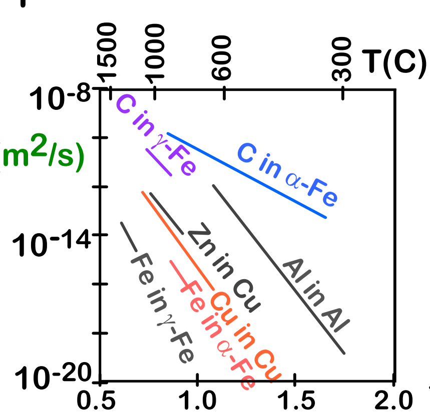
pre-exponential [m^2/s] (see Table 5.2, *Callister 6e*)

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:



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.)

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

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

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Diffusion Coefficient

Table 5.2 A Tabulation of Diffusion Data

Diffusing Species	Host Metal	$D_0 (m^2/s)$	Activation Energy Q_d kJ/mol	Activation Energy Q_d eV/atom	Calculated Values T(°C)	Calculated Values $D (m^2/s)$
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.

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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_o and C_s.

- Result: Dt should be held constant.

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

- Answer:

$$t_{500} = \frac{(\overset{5.3\text{x}10^{-13}m^2/s}{D}\,\overset{10hrs}{t})_{600}}{\underset{4.8\text{x}10^{-14}m^2/s}{D_{500}}} = 110hr$$

Note: values of D are provided here.

SUMMARY: STRUCTURE & DIFFUSION

Diffusion FASTER for...

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

Diffusion SLOWER for...

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