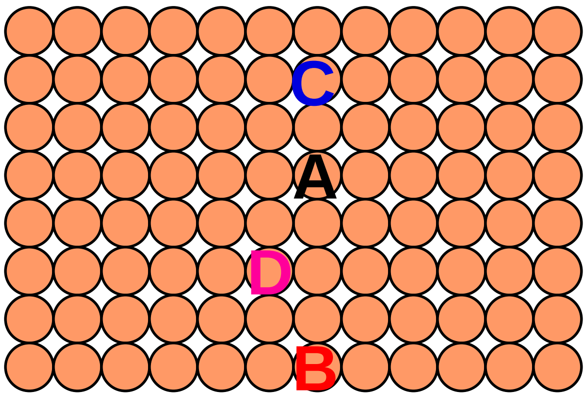
Announcements

- Welcome to the Wong Building!
- Ch. 4 solutions will be posted to WebCT on Friday.
- The deadline for WebCT quizzes is *extended*. You will have from the time it is posted until **~~7~~ PM on** 9PM **Fridays**.
- Ch. 5 homework: 5.1, 5.2, 5.3, 5.8, 5.14, 5.23, 5.10, 5.11, 5.21, 5.28 plus one additional problem (see the problem set file on WebCT).

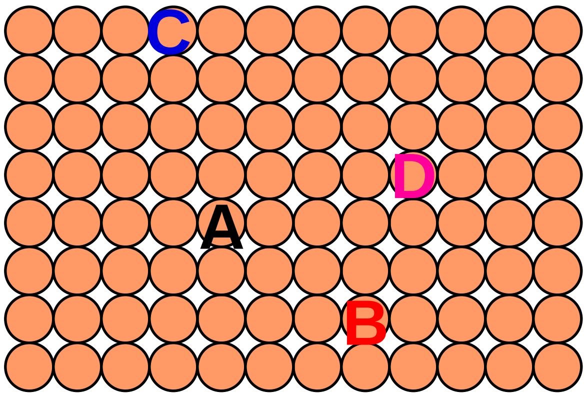
Diffusion

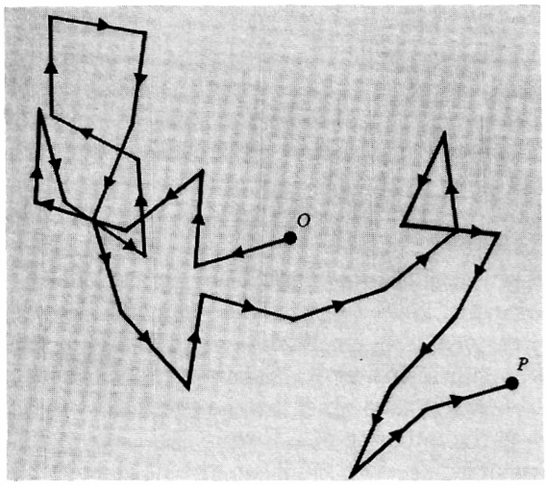
- Self-diffusion: In an elemental solid, atoms also migrate.

Label some atoms



After some time





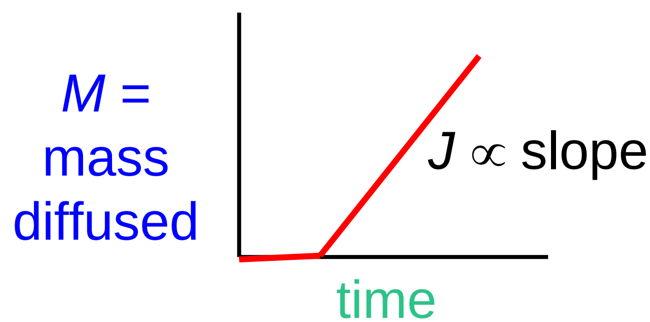
Diffusion

- **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**

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



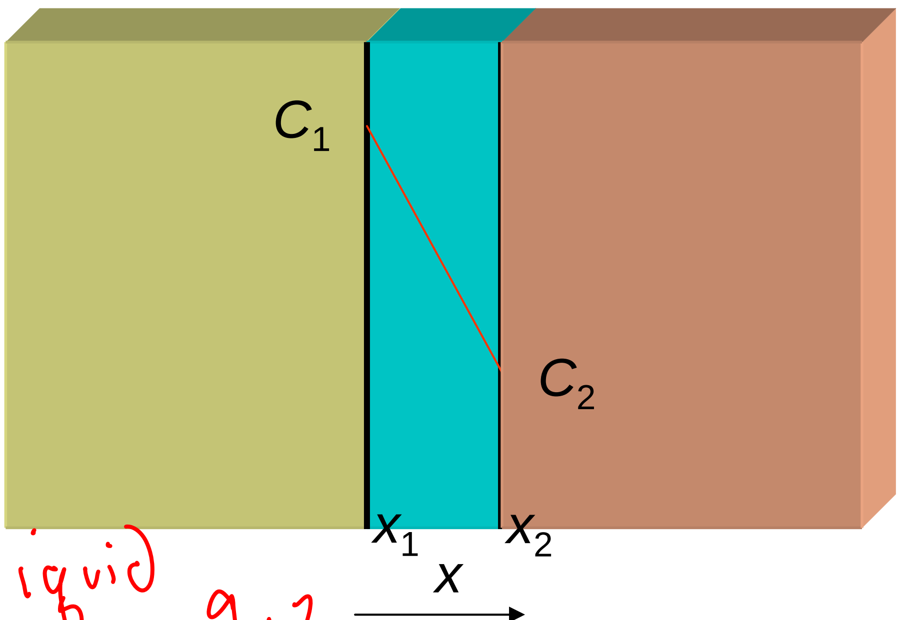
Steady-State Diffusion

1855

Rate of diffusion independent of time

Flux proportional to concentration gradient = $\frac{dC}{dx}$

atom/m^3



Liquid $10^{-9}\ m^2/s$

Fick's first law of diffusion

$$\boxed{J = -D\frac{dC}{dx}}$$

$\frac{\text{atoms}}{m^2 s}$ $\qquad$ m^2/s $\qquad$ $\frac{1}{m}\,\frac{\text{atom}}{m^3}$

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

$D \equiv$ diffusion coefficient

$10^{-12}\ m^2/s \longleftrightarrow 10^{-26}\ m^2/s$

S.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:**

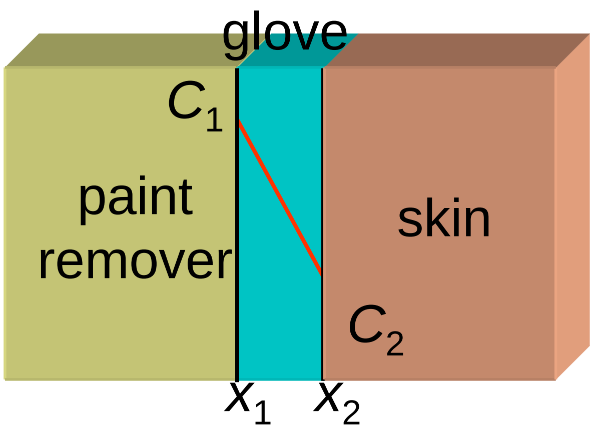
    $$\boldsymbol{D} = 110 \times 10^{-8}\ \mathrm{cm^2/s}$$

  - **surface concentrations:**

$$C_1 = 0.44\ \mathrm{g/cm^3}$$
$$C_2 = 0.02\ \mathrm{g/cm^3}$$

Example (cont).

- Solution – assuming linear conc. gradient



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

Data:

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

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

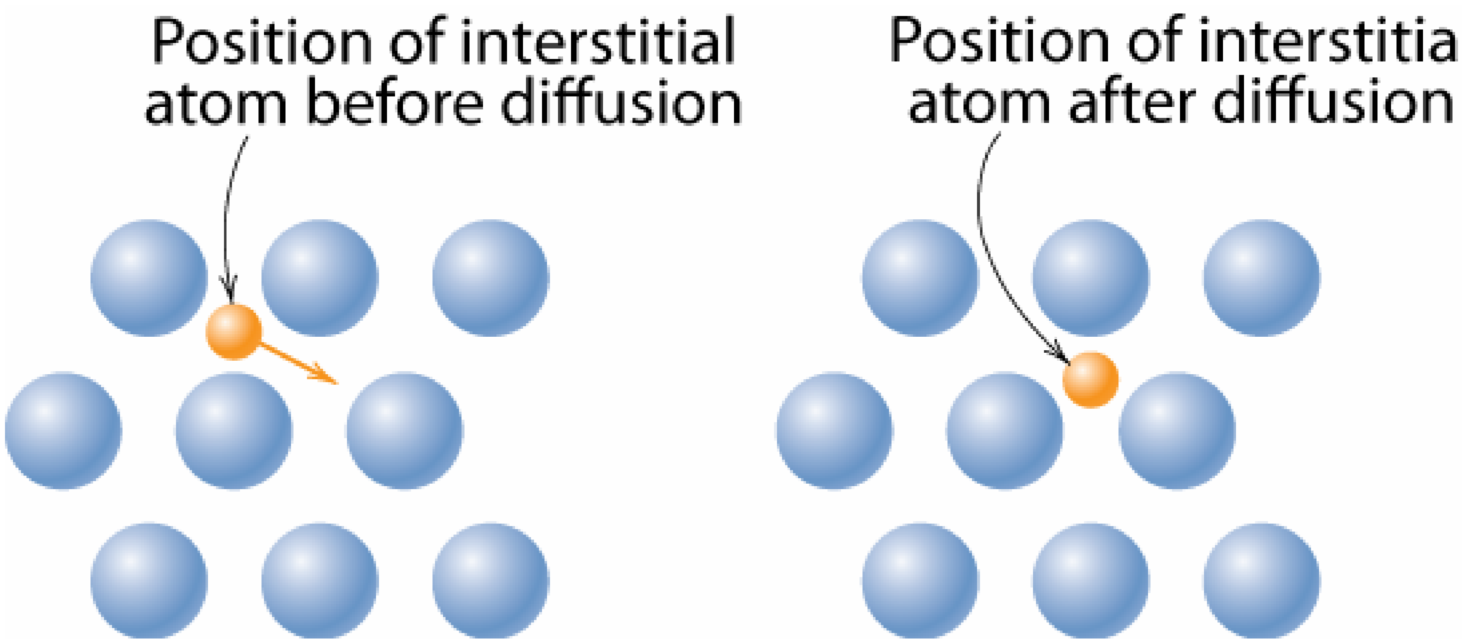
$C_2 = 0.02\ \mathrm{g/cm^3}$

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

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

Diffusion Mechanisms

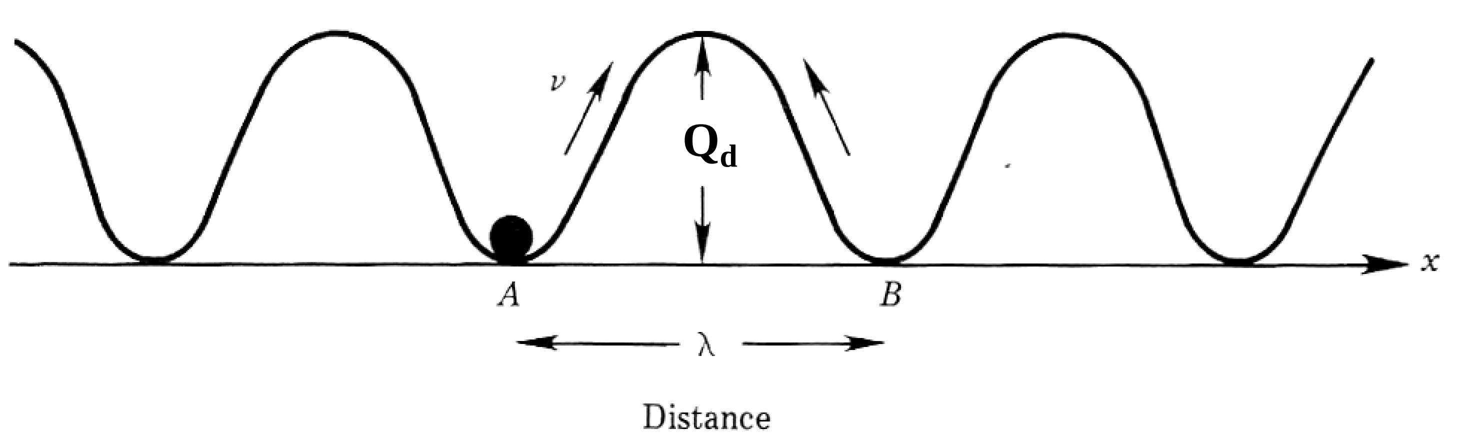
- **Interstitial diffusion – smaller atoms can diffuse between atoms.**

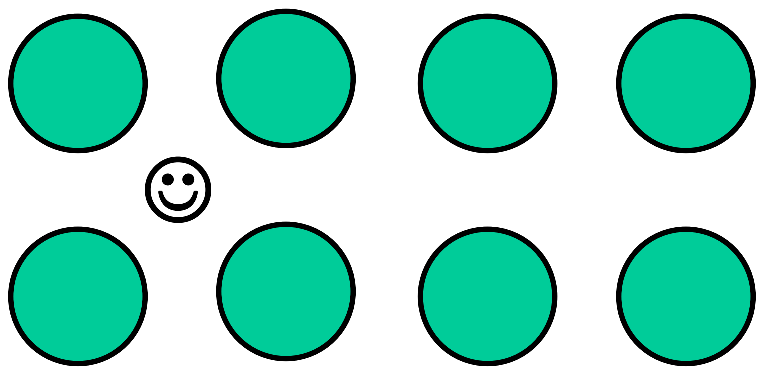


Adapted from Fig. 5.3 (b), *Callister 7e*.

More rapid than vacancy diffusion

Diffusion and Activation Barrier





Diffusion and Temperature

- Diffusion coefficient increases with increasing *T*.

E_a

ΔH

$$D = D_o \exp\left(-\frac{Q_d}{RT}\right) \quad \textbf{OR} \quad D = D_o \exp\left(-\frac{Q_d}{k_b T}\right)$$

D = diffusion coefficient [m^2/s] or sometimes [cm^2/s]

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

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

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

k_b = Boltzmann's constant [8.617x10^{-5} eV/atom-K]

T = absolute temperature [K]

Diffusion coefficient, D (units? m^2/s)

$$D = \nu \lambda^2 = \underbrace{\boxed{\nu_o \lambda}}_{D_o} \exp\left(-\frac{Q}{k_B T}\right)$$

What does D depend on

1. λ jump distance → crystal structure
2. ν_o vibrational frequency "Debye"
3. T — T increases D increase
4. Q — if Q increases D decrease
5. Diffusion mechanism

$$J = -D \frac{\partial c}{\partial x}$$

Physics

driving force

$$E \leftarrow \frac{\partial V}{\partial x}$$

voltage

electromigration

"special topic"

Fe-C example

interstitial

$$D = \frac{1}{6}\nu\lambda^2$$

γ Fe $a = 0.37$ nm

$\lambda = a/\sqrt{2} = 0.26$ nm

D varies with composition; e.g.

C diff coeff in 0.15%C steel at 1000 °C $=2.5\times10^{-11}\ m^2s^{-1}$

in 1.4%C $=7.7\times10^{-11}\ m^2s^{-1}$

Because of lattice distortion

$\therefore\ \nu = 2\times10^{9}$ jumps/sec

$\nu_0 = 10^{13}$ vibration/sec

1 out 10^4 attempts is successful

Net displacement vs. prediction of D alone

Fe - C

C diffusion @ 1000°C $D = 2.5 \times 10^{-11}\ m^2/s$

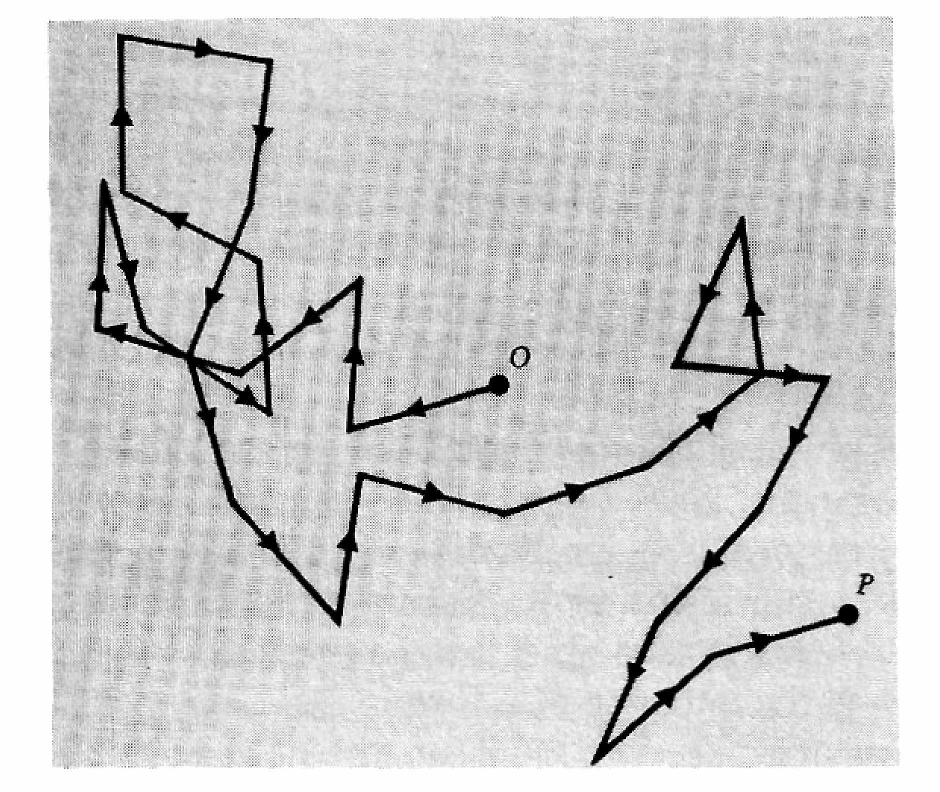
(0.15% C)

We said this resulted in 2×10^9 jumps/s

$t = 1$ sec $\lambda = 0.26$ nm

Total ~~total~~ distance is ~ 0.5 m

RANDOM WALK



$D(m^2/s) \to \nu \lambda^2$

ν = Freq of jump × time

RANDOM WALK?

Net displacement for n jumps will be $\lambda\sqrt{n}$

Net disp $= \lambda\sqrt{\nu t}$

" $= \sqrt{Dt}$

Net displacement vs. prediction of D alone

Fe - C

C diffusion @ 1000°C $D = 2.5 \times 10^{-11}\ m^2/s$

(0.15% C)

We said this resulted in 2×10^9 jumps/s

$t = 1$ sec $\lambda = 0.26$ nm

Total total distance is 0.5 m crazy

However this a RANDOM WALK!

Net disp. $= \sqrt{Dt}$

$\cong 5 \times 10^{-6}$ m $\rightarrow$ $\boxed{5\ \mu m}$

TYPES OF DIFFUSION COEFFICIENTS

1. Self-diffusion coefficient

   Fe in Fe, Cu in Cu

2. Solute diffusion coefficient

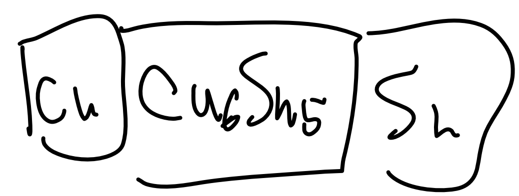
   C in Fe, Cu in Si

   Cu in Cu_6Sn_5

   Si in Cu_3Si

3. Interdiffusion coefficient

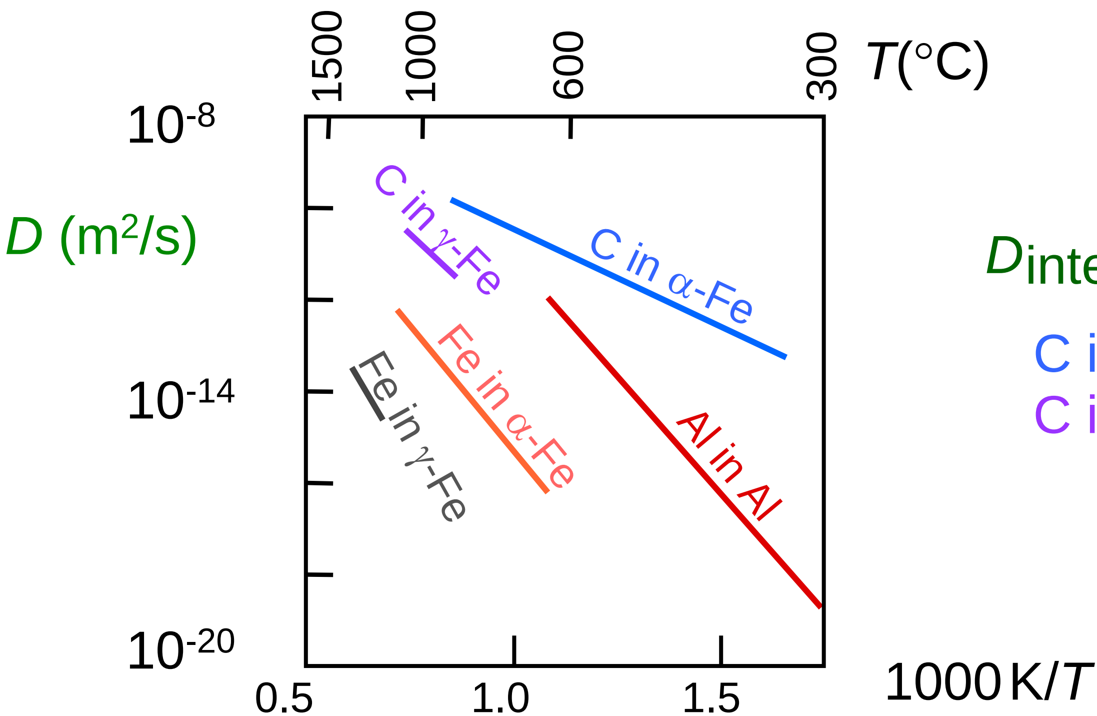
$$\tilde{D} = X_{Cu} D_{Sn} + X_{Sn} D_{Cu}$$



$$\tilde{D} \rightarrow Cu_6Sn_6$$

Diffusion and Temperature

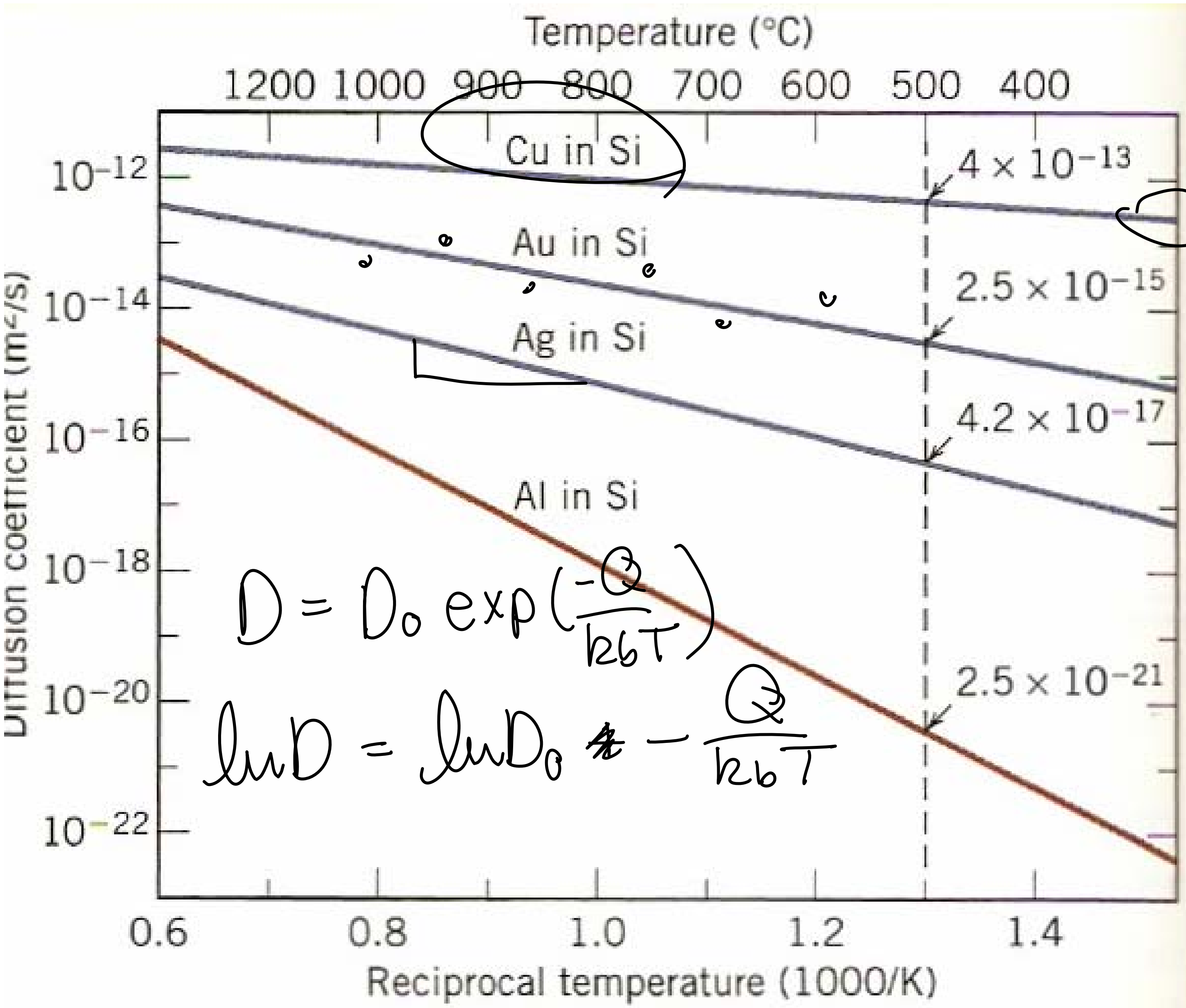
D has exponential dependence on *T*



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

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

Adapted from Fig. 5.7, *Callister 7e*. (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.)



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

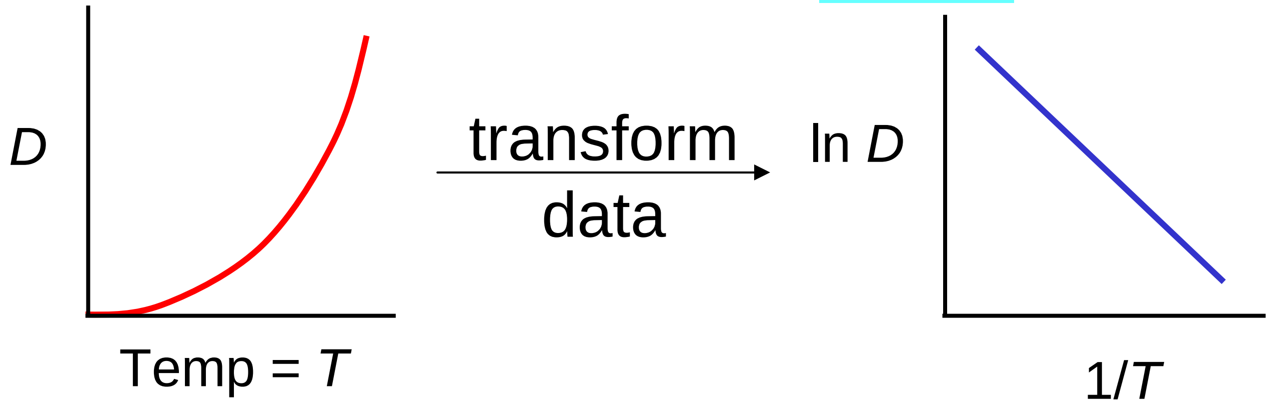
$$\ln D = \ln D_0 - \frac{Q}{k_b T}$$

Example: At 500ºC the diffusion coefficient and activation energy for Cu in Si are

$D(500ºC) = 4 \times 10^{-13}\ \text{m}^2/\text{s}$

$Q_d = 41.5$ kJ/mol

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.)

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

$T_1 = 273 + 500 = 773\,K$

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

500°C

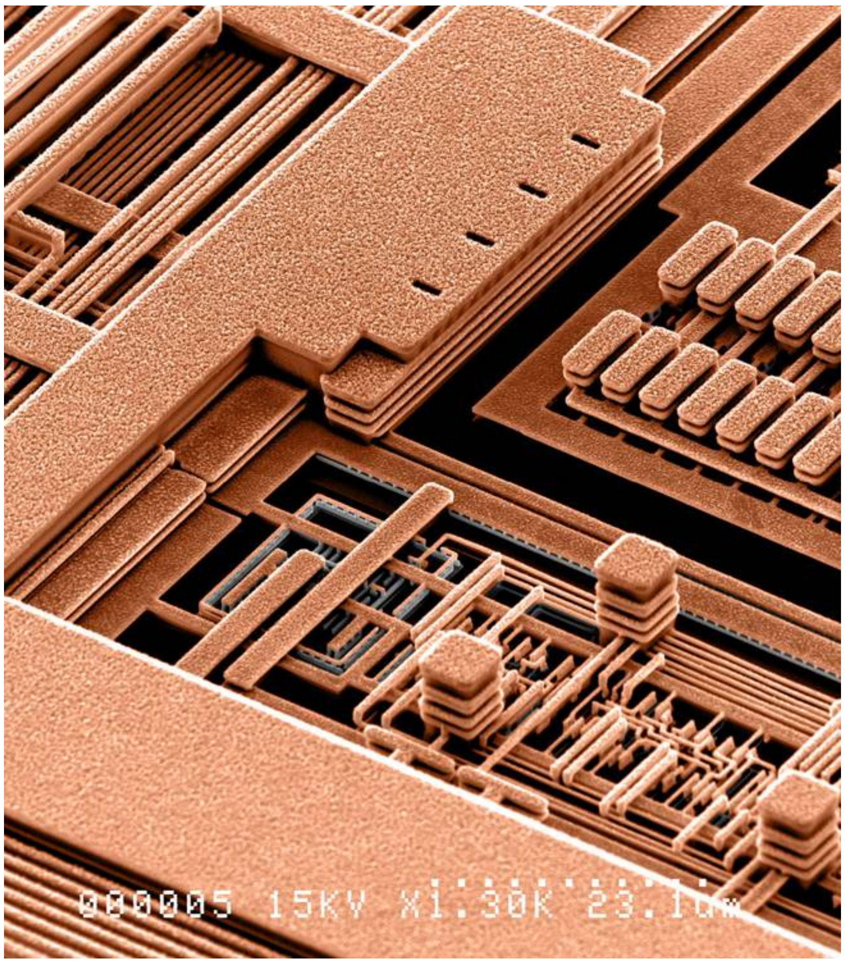
$$D_2 = (4 \text{ x } 10^{-13} \text{ m}^2/\text{s}) \exp\left[\frac{-41{,}500 \text{ J/mol}}{8.314 \text{ J/mol-K}}\left(\frac{1}{623\text{ K}} - \frac{1}{773\text{ K}}\right)\right]$$

350°C

$$\boxed{D_2 = 0.84 \text{ x } 10^{-13} \text{ m}^2/\text{s}}$$

$\left\{\frac{Cu}{Si}\right\} \rightarrow$ "Proprietary" "Diffusion Barrier"

Cu Interconnects



- Cu diffuses readily into Si
- Most chips require an elevated temperature processing step
- How do we manage to use Cu for integrated circuits?

Non-steady State Diffusion

- **The concentration of diffusing species is a function of both time and position $C = C(x,t)$**
- **In this case Fick's Second Law is used**

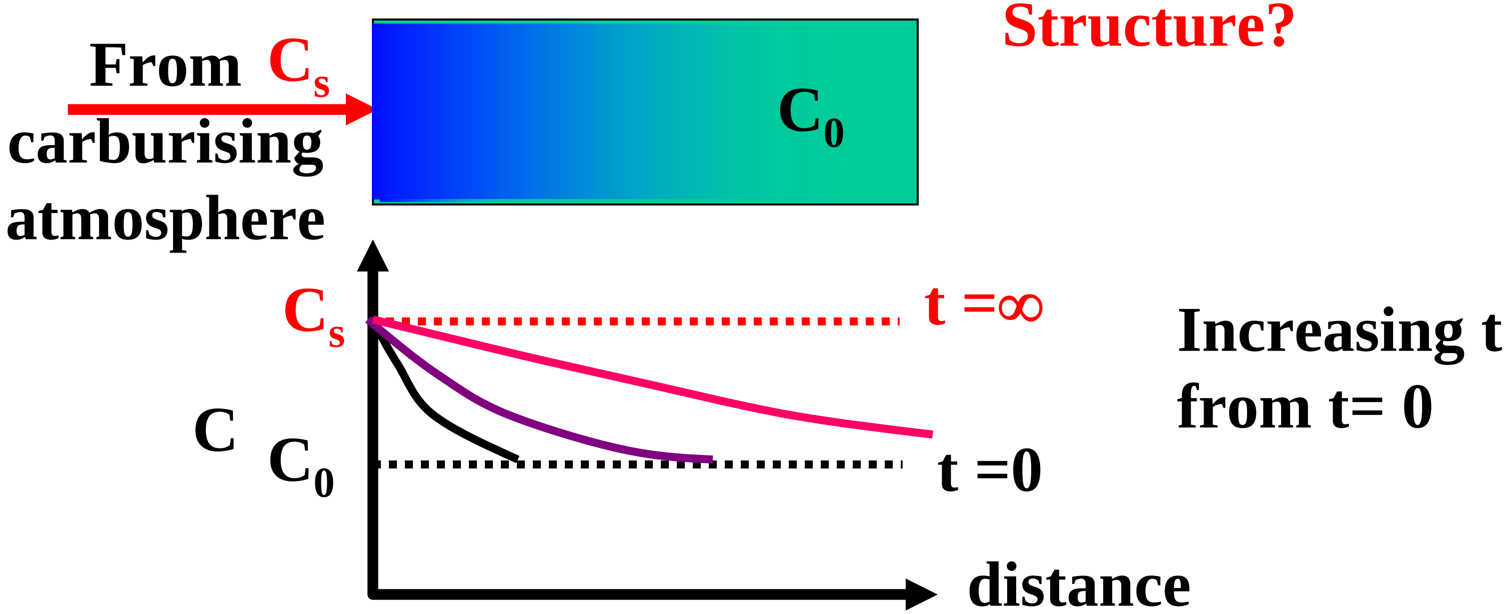
Fick's Second Law $$\boxed{\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}}$$

Applications of Ficks 2nd law

The Carburization of Steel

increase in C concn to increase surface hardness/wear resistance

Structure?



Require time to reach certain C concn to certain depth

solve Ficks 2nd law using following boundary conditions

at x=0, $C_B=C_s$ at x=∞ $C_B=C_0$

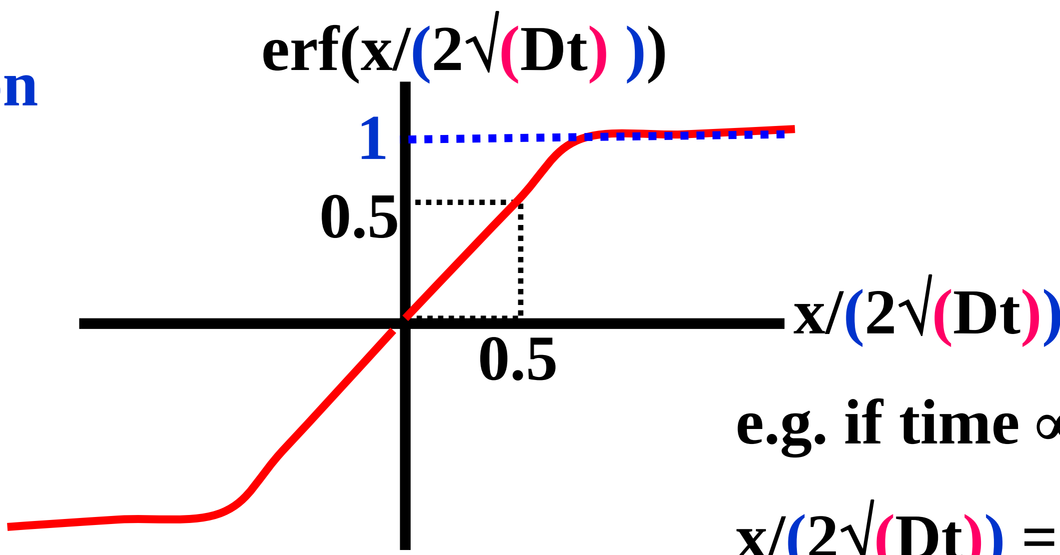
$$\frac{C(x,t)-C_o}{C_s-C_o} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Solution

D varies with C%

Take avg value

Error function



e.g. if time ∞,

$x/(2\sqrt{(Dt)}) = 0$,

and $C=C_s$ throughout the specimen