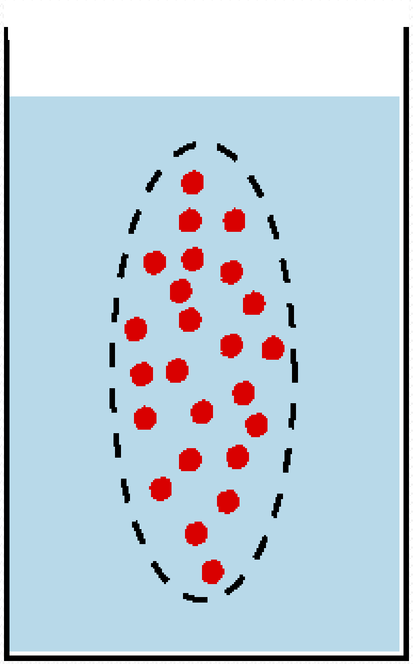
CHAPTER 5:
DIFFUSION IN SOLIDS

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: DEFINITIONS

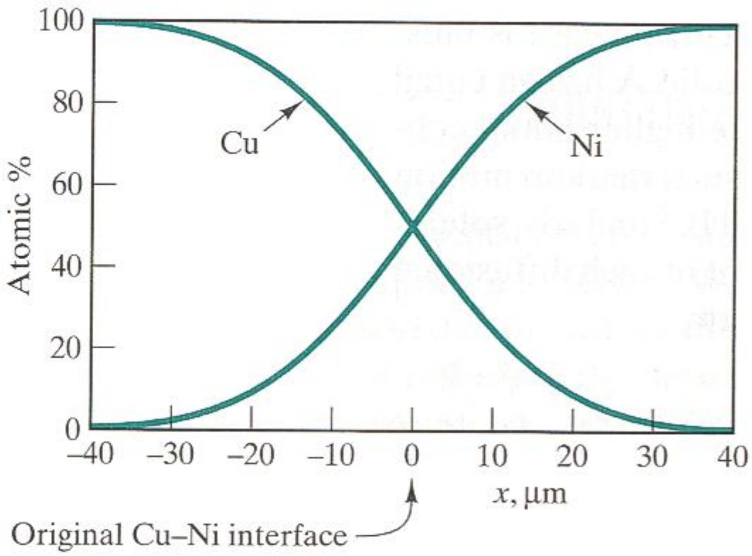


- Diffusion is a process of ***mass transport*** that involves **atomic motion.**
- In the simplest form, the diffusion can be defined as the ***random walk*** of an **ensemble of particles** from regions of high concentration to regions of lower concentration.

Diffusion

In each diffusion process (heat flow, for example, is also a diffusion process), the flux (of matter, heat, electricity, etc.) follows the general relation:

Flux = (Conductivity) x (Driving Force)



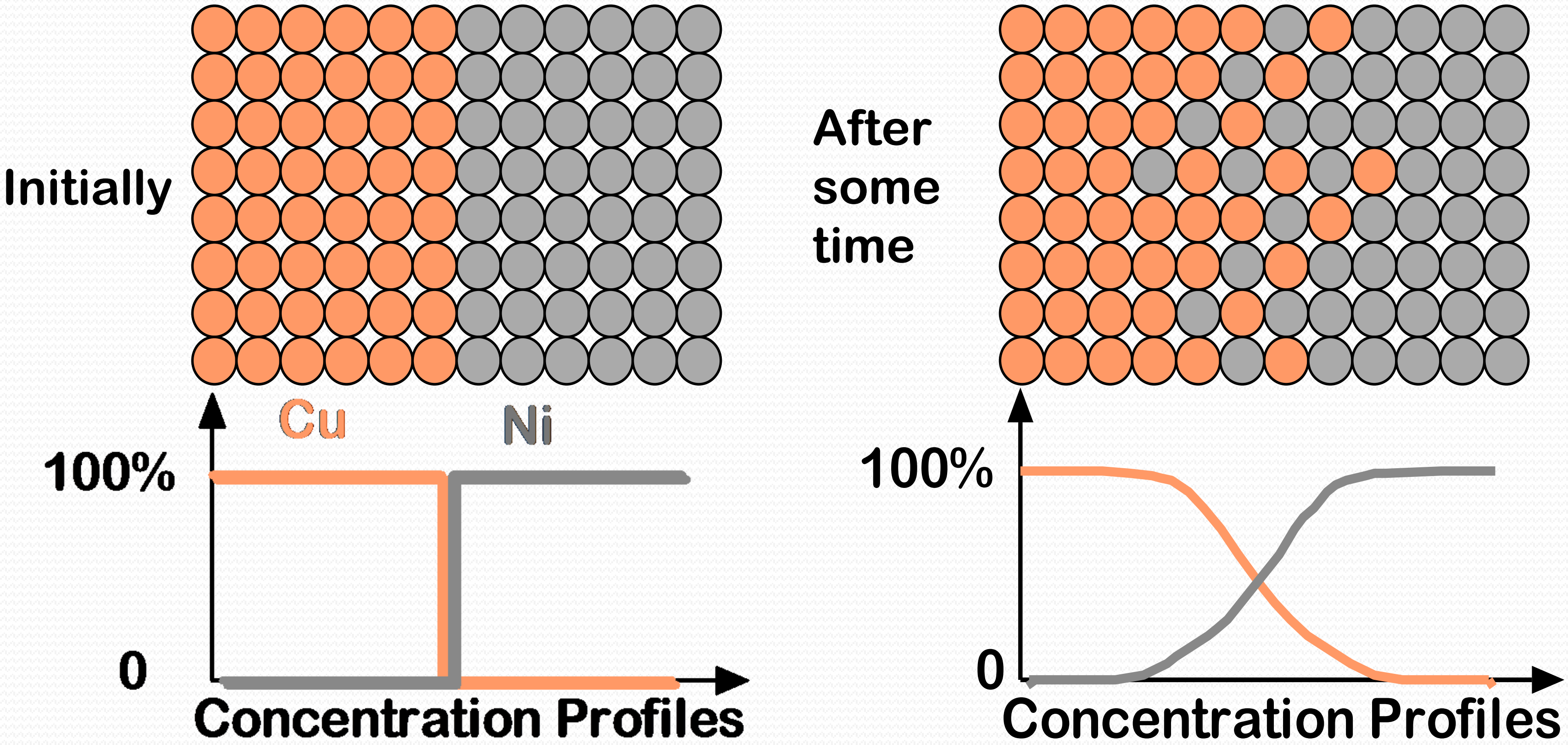
- In the case of atomic or molecular diffusion, the "**conductivity**" is referred to as the **diffusivity or the diffusion constant**, and is represented by the symbol D, which reflects the **mobility** of the diffusing species in the given environment. Accordingly one can assume larger values in gases, smaller ones in liquids, and extremely small ones in solids.

- The "**driving force**" for many types of diffusion is the existence of a **concentration gradient**. The term "gradient" describes the variation of a given property as a function of distance in the specified direction.

DIFFUSION: THE PHENOMENA

- **Interdiffusion**: atoms tend to migrate from regions of large concentration.

Cu-Ni diffusion couple



- Diffusion in solids is **material transport by atomic motion**.
- **Inhomogeneous** materials can become **homogeneous** by diffusion.
- For an active diffusion to occur, the **T** should be high enough to overcome **energy barriers** to atomic motion.

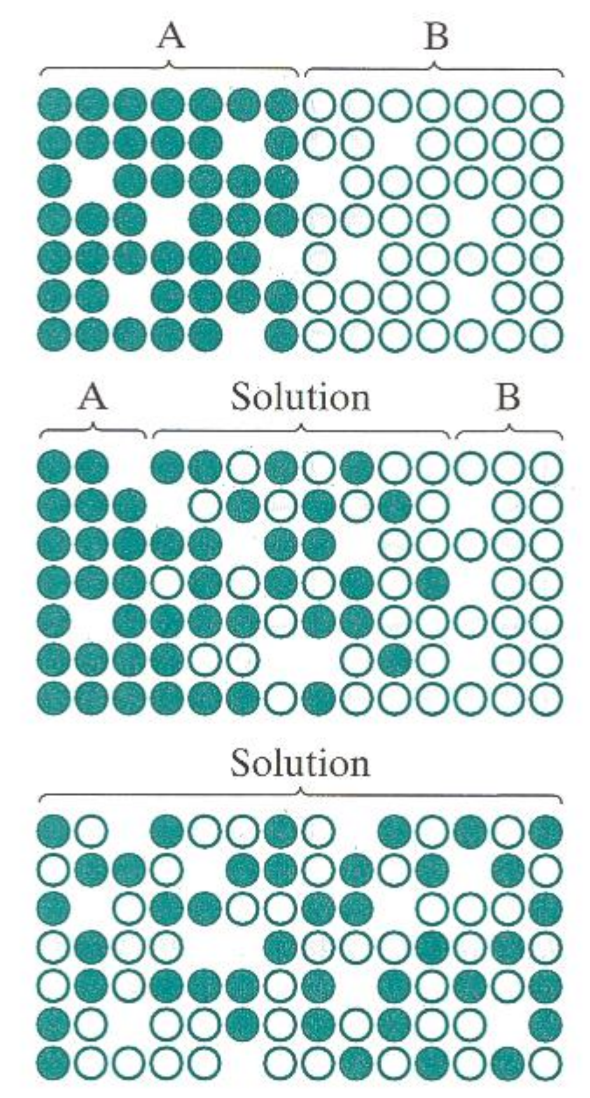
DIFFUSION MECHANISMS

- The energy requirements to squeeze the most atoms or ions through ***perfect crystalline*** structures are so high as to make ***diffusion*** nearly ***impossible***

- To make solid-diffusion practical, ***point defects*** (e.g. vacancies) are generally required
- Or/and migrating atoms that are ***small*** enough to fit into the ***interstitial*** positions

There are two main mechanisms for diffusion.

VACANCY MIGRATION MECHANISM

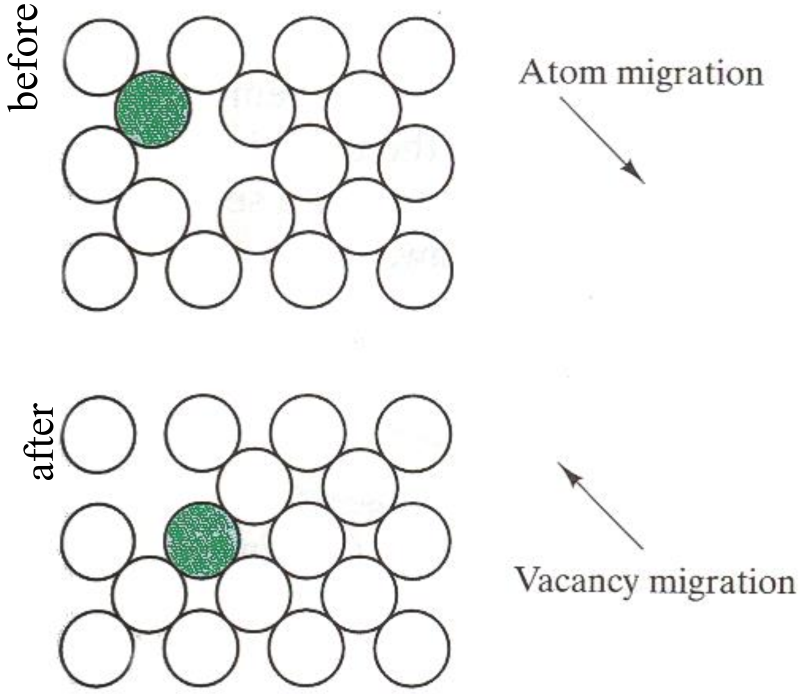


- Any given A and B atoms is **equally likely** to "walk" in **any random direction**

- but the **concentration gradients** of the two materials can result in a **net flow** of A to B and vice versa

VACANCY MIGRATION MECHANISM

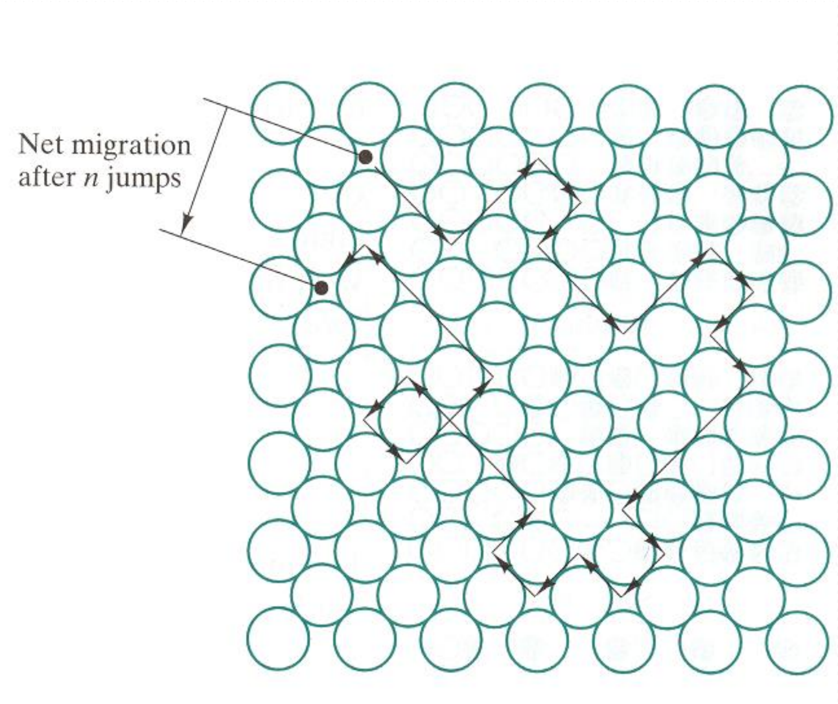
- applies to **substitutional impurities**



- atoms exchange with vacancies and the overall direction of materials flow is opposite to the direction of vacancy flow

- diffusion rate depends on:
  - --number of vacancies
  - --activation energy to exchange

INTERSTITIAL DIFFUSION MECHANISM



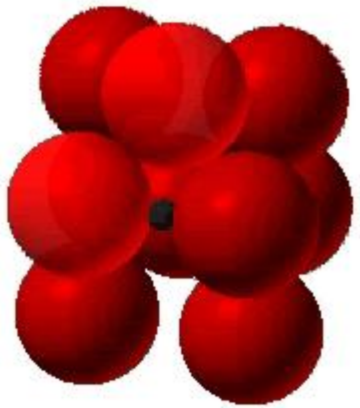
- Applies to **interstitial** impurities

- Note the **random** walk nature of atomic migration. But again this randomness **does not preclude** the **net flow** of material when there is an overall **variation** in chemical **composition**

INTERSTITIAL SIMULATION

- 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.

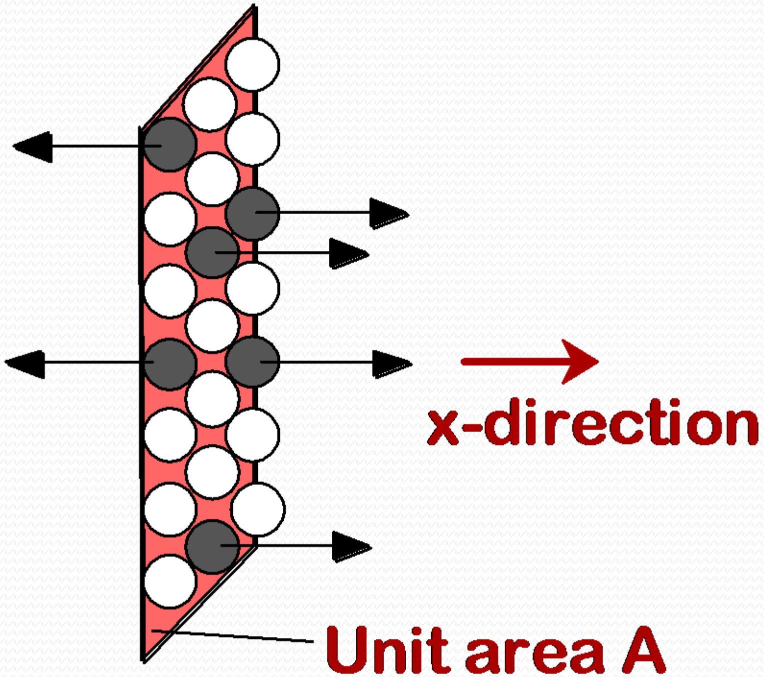


(Courtesy P.M. Anderson)

MODELING DIFFUSION: FLUX

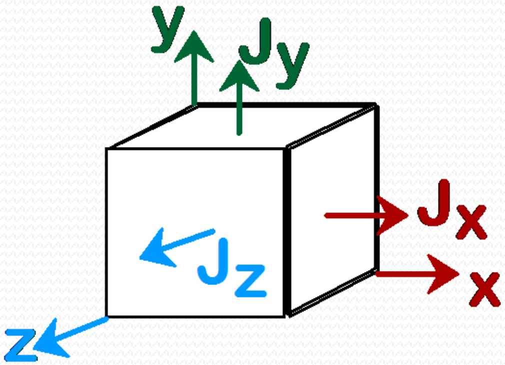
- **Diffusion Flux (J) defines the mass transfer rate:**

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



Unit area A through which atoms move.

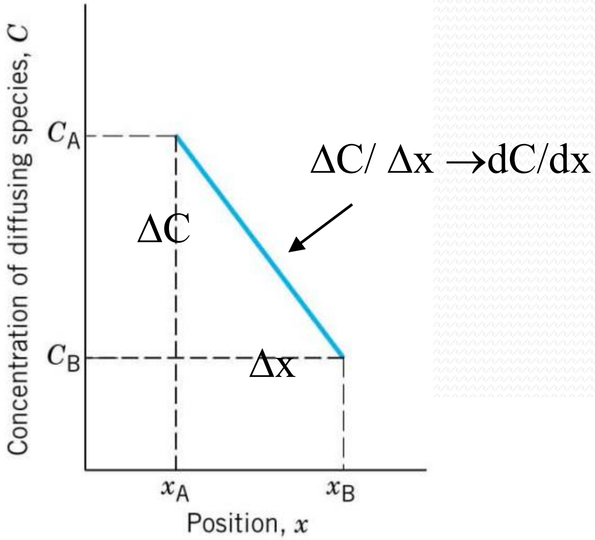
- Directional Quantity

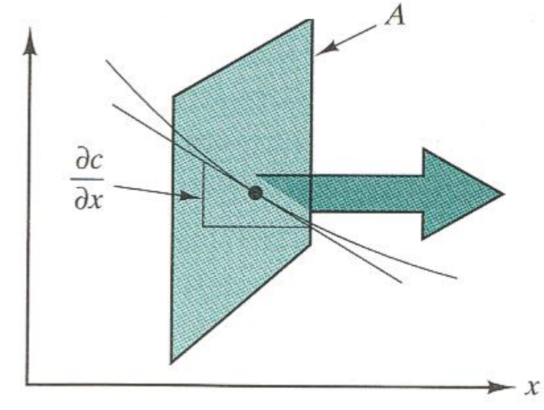


- Flux can be measured for:
  - --vacancies
  - --host (A) atoms
  - --impurity (B) atoms

STEADY-STATE DIFFUSION (Fick's First Law)

SSD takes place at constant rate. It means that throughout the system dC/dx=const and dC/dt=0





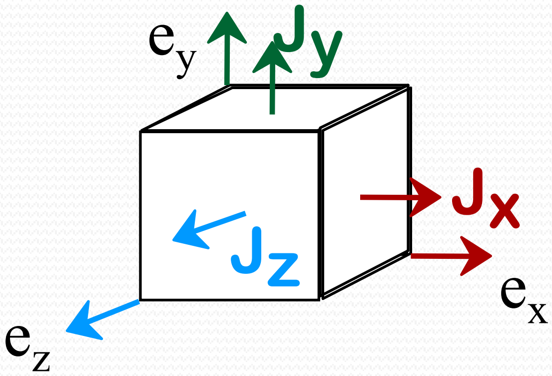
$$\mathbf{J} = -\mathbf{D} \cdot \left(\frac{\partial \mathbf{c}}{\partial \mathbf{x}}\right)$$ - Fick's first law

The diffusion flux is proportional to the existing concentration gradient

FIRST FICK's LAW

$$\vec{\mathbf{J}} = -\mathbf{D} \cdot \mathbf{grad}\, \mathbf{C} = -\mathbf{D}\left(\frac{\partial \mathbf{C}}{\partial \mathbf{x}} \vec{\mathbf{e}}_{\mathbf{x}} + \frac{\partial \mathbf{C}}{\partial \mathbf{y}} \vec{\mathbf{e}}_{\mathbf{y}} + \frac{\partial \mathbf{C}}{\partial \mathbf{z}} \vec{\mathbf{e}}_{\mathbf{z}}\right)$$

where D is the **diffusion coefficient** [m^2/s]
and C is a concentration [kg/m^3]



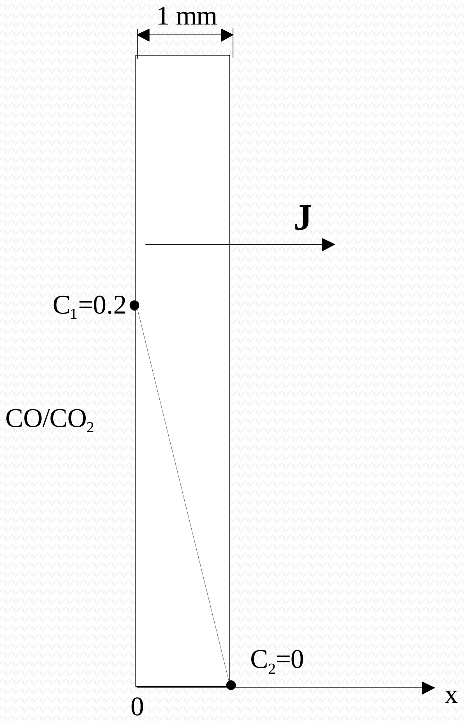
$$D=D_0\exp(-Q_d/RT)$$

here Q is the activation energy for the process: [J/mol];
D_o is temperature-independent pre-exponential constant: [m^2/s]

Problem: STEADY STATE DIFFUSION

- Hardening of steel surface by carburizing process.

Assume that a thin (1mm) plate of BCC Fe (density ~7.9 g/cm^3) is heated to 1000 K. One side of the plate is in contact with CO/CO$_2$ gas mixture that maintains the carbon concentration at the surface at 0.2 wt.%. The other side has no contact with oxidizing atmosphere that maintains the surface concentration at 0 wt.%. Compute the number of carbon atoms transported to the back surface per second and area 1 cm^2.
(D=8.7 10^{-7} cm^2/s at T=1000 K)



$$C_n = \left(\frac{\text{wt.\%C} \cdot \text{Density of Fe}}{\text{Mol.wt. C}} \right) \cdot (\text{Avogadro's Number})$$

$$C_1 = \left(\frac{(0.002) \cdot 7.9\,\text{g}/\text{cm}^3}{12.01\,\text{g}/\text{mol}} \right) \cdot (6.02 \cdot 10^{23}\,\text{atoms}/\text{mol}) = 7.92 \cdot 10^{20}\,\text{atoms}/\text{cm}^3$$

$$C_2 = 0$$

The concentration gradient is then :

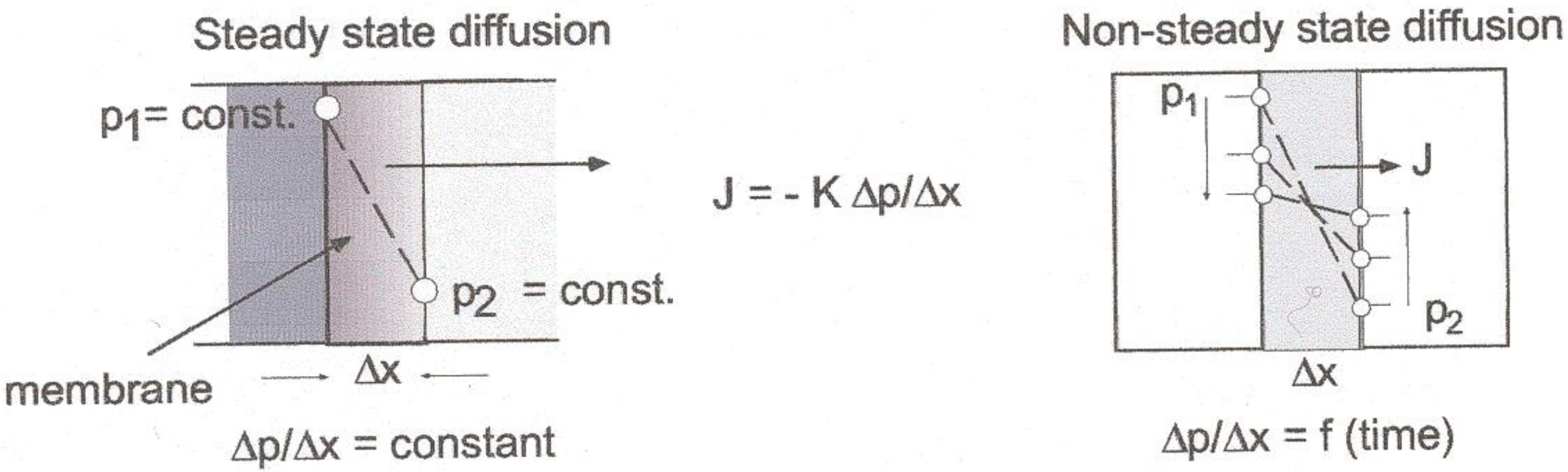
$$\frac{dC}{dx} \approx \frac{C_2 - C_1}{\text{Sample thickness}} = -\frac{7.92 \cdot 10^{20}\,\text{atoms}/\text{cm}^3}{0.1\text{cm}} = 7.92 \cdot 10^{21}\,\text{atoms}/\text{cm}^2$$

Finally :

$$J = -D\left(\frac{dC}{dx}\right) = (8.7 \cdot 10^{-7}\,\text{cm}^2/\text{s}) \cdot (7.92 \cdot 10^{21}\,\text{atoms}/\text{cm}^2) = 6.9 \cdot 10^{15}\,\text{atoms}/\text{cm}^2\text{s}$$

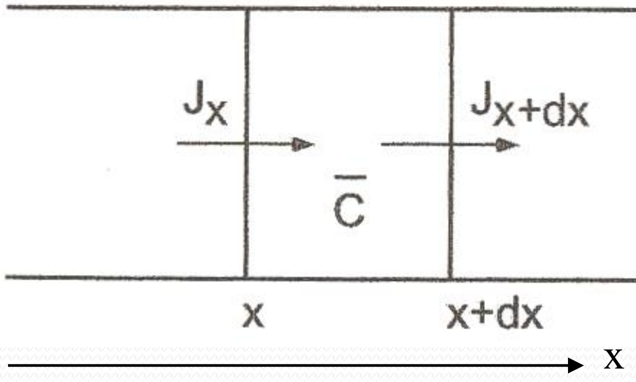
NONSTEADY-STATE DIFFUSION

- Concentration profile, C(x), changes with time: $dC/dt \neq 0$.



<u>Example:</u> diffusion from a finite volume through a membrane into a finite volume. The pressures in the reservoirs involved change with time as does, consequently, the pressure gradient across the membrane.

FICK's SECOND LAW



Consider a volume element (between x and x+dx of unit cross section) in a diffusion system. The flux of a given material into a volume element (J_x) minus the flux out of the element volume (J_{x+dx}) equals the rate of material accumulation in the volume:

$$\boxed{J_x - J_{x+dx} = \frac{\partial \overline{C}}{\partial t} \cdot dx}$$

$\overline{C}$ is the average species concentration in the volume element

Using a Taylor series we can expand J_{x+dx}:

$$J_{x+dx} = J_x + \frac{\partial J_x}{\partial x} dx + \frac{1}{2} \frac{\partial^2 J_x}{\partial x^2} dx^2 + \ldots$$

Accordingly, as dx→0 and using Fick's First Law:

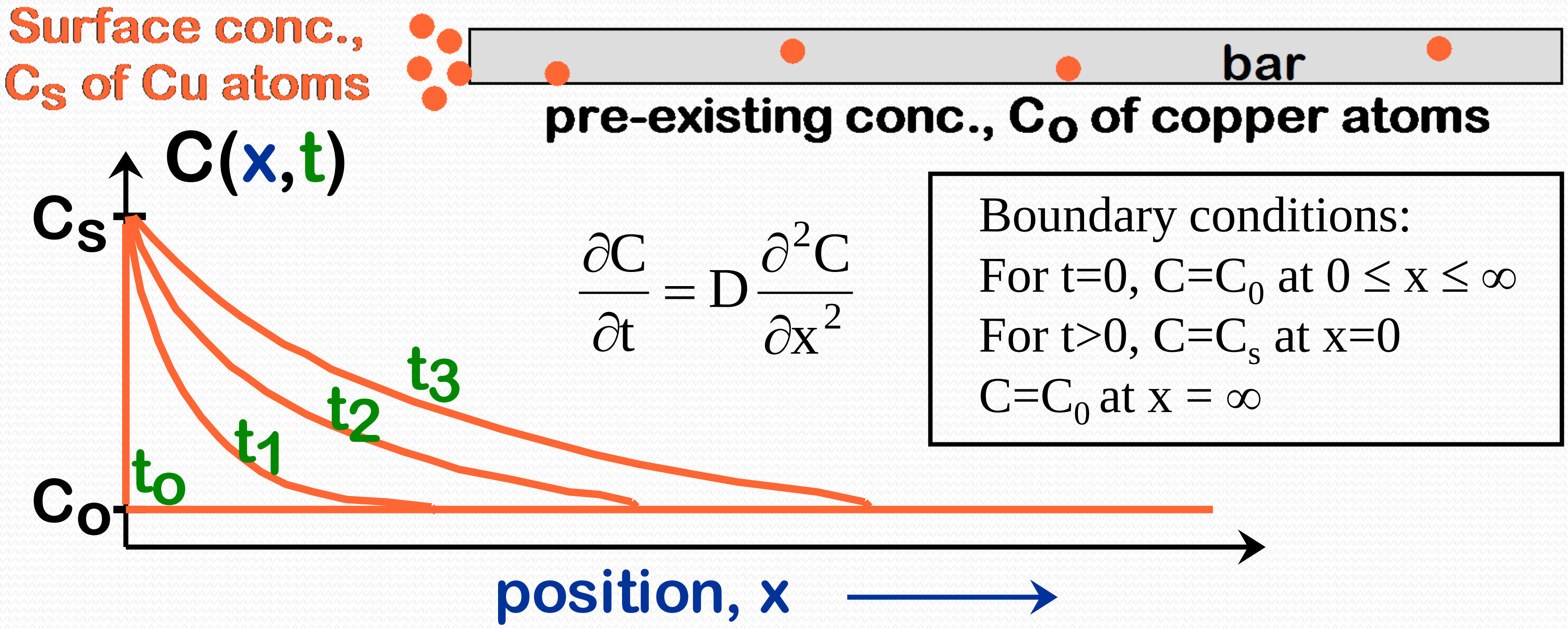
$$\frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x}\right) = \frac{\partial C}{\partial t}$$

And if D does not vary with x we have The formulation of ***Fick's Second Law***:

$$\boxed{\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}}$$

Problem: NON STEADY STATE DIFFUSION

- Copper diffuses into a ***semi-infinite*** bar of aluminum.



$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Boundary conditions:
For t=0, $C=C_0$ at $0 \le x \le \infty$
For t>0, $C=C_s$ at x=0
$C=C_0$ at $x = \infty$

- General solution:

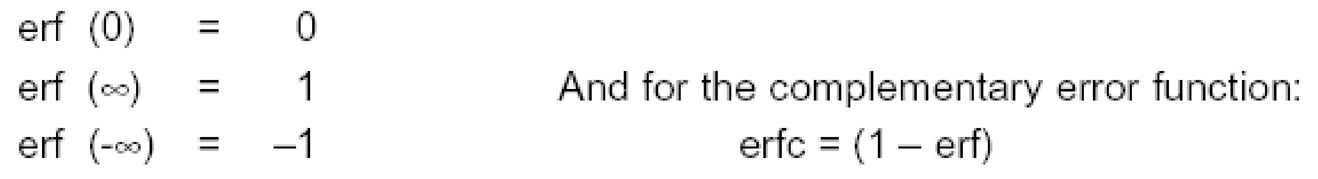
$$\boxed{\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)}$$

Error Function

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2}\,dy \qquad z = x/2\sqrt{Dt}$$

- The terms erf and erfc stand for **error function** and complementary error function respectively - it is the Gaussian error function as tabulated (like trigonometric and exponential functions) in mathematical tables. (see Table 5.1, *Callister 6e)*.

- Its limiting values are:



$\operatorname{erf}(0) = 0$

$\operatorname{erf}(\infty) = 1$

$\operatorname{erf}(-\infty) = -1$

And for the complementary error function:

erfc = (1 – erf)

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.

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

- **Answer:**

$$t_{500} = \frac{(\overset{5.3\times10^{-13}m^2/s}{D}\,\overset{10hrs}{t})_{600}}{\underset{4.8\times10^{-14}m^2/s}{D_{500}}} = 110hr$$

Note: values of D are provided here.

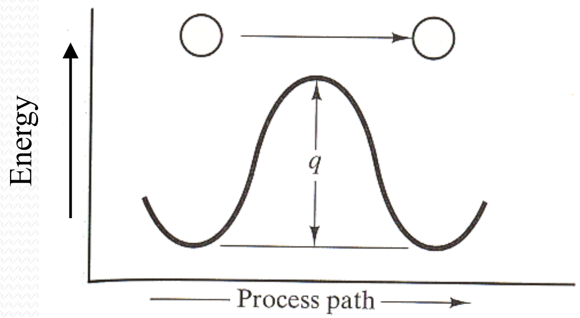
THERMALLY ACTIVATED PROCESSES

Examples: rate of creep deformation, electrical conductivity in semiconductors, the ***diffusivity*** of elements in metal alloy

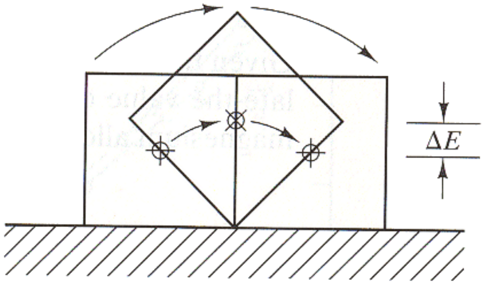
Arrhenius Equation

$$\text{Rate} = K \cdot \exp(-Q/RT)$$

where K is a ***pre-exponential constant*** (independent of temperature),
Q- the ***activation energy***, R the universal gas constant and T the absolute temperature

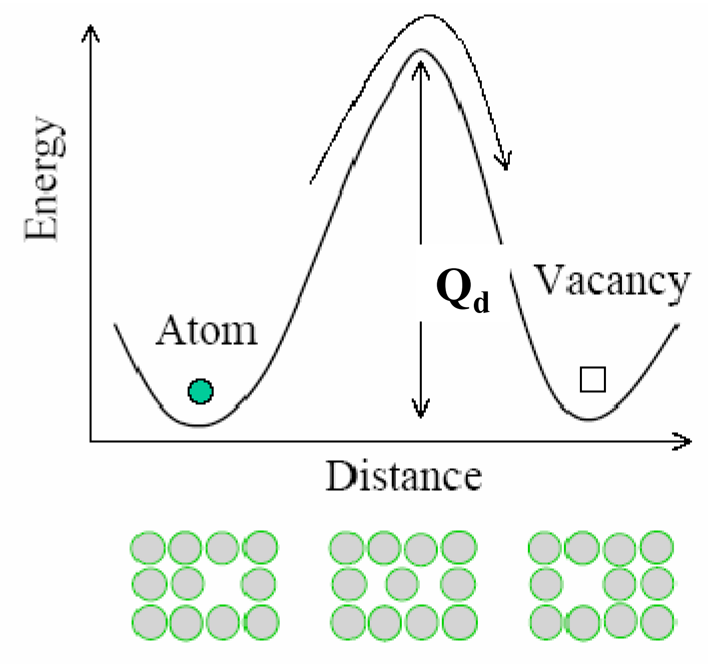


Atom must overcome an activation energy q, to move from one stable position to another



Mechanical analog: the box must overcome an increase in potential energy ΔE, to move from one stable position to another

DIFFUSION in SOLIDS is thermally activated process

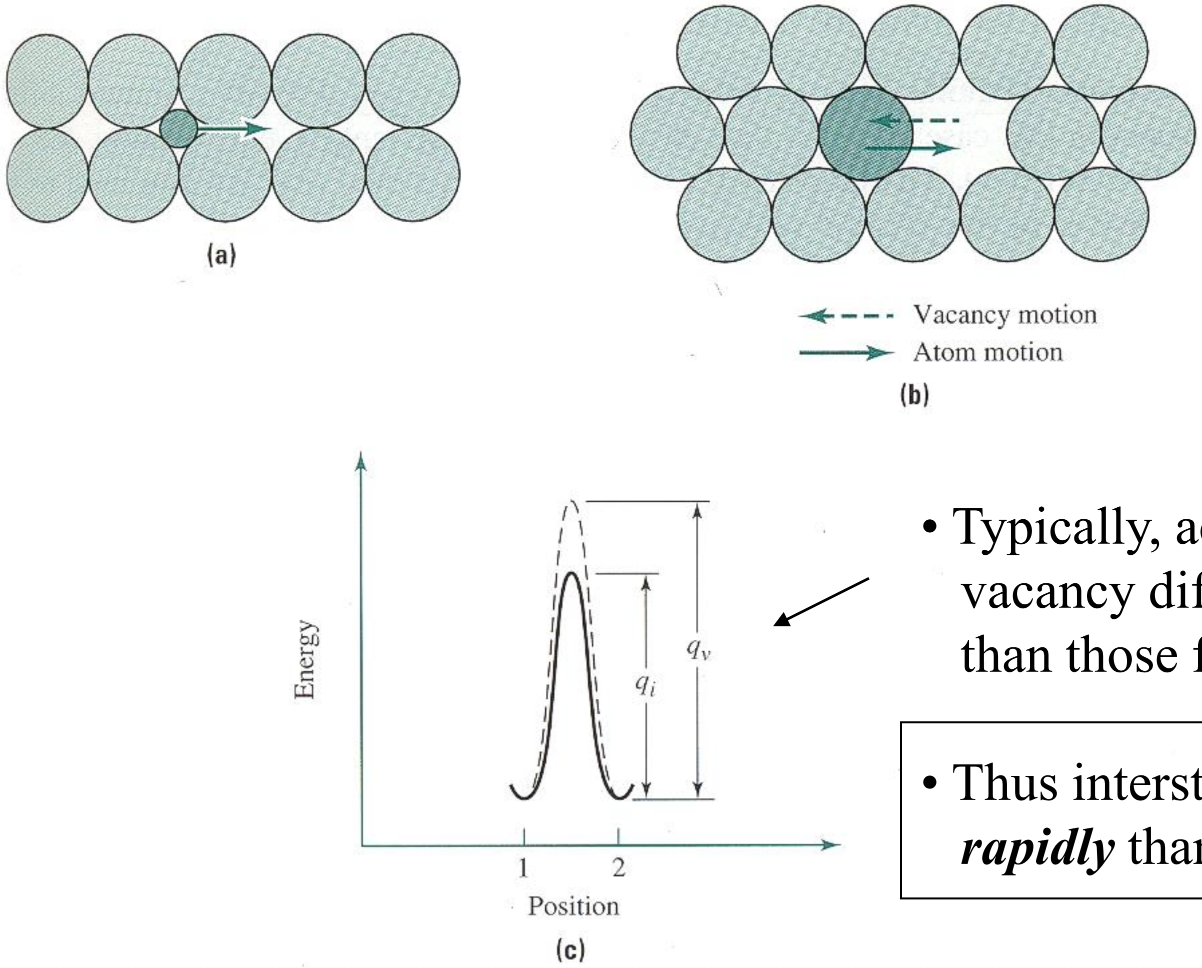


Schematic representation of the diffusion of an atom from its original position into a vacant lattice site. At activation energy Q_d has to be supplied to the atom so that it could break inter atomic bonds and to move into the new position.

- In order atom can jump along the solid body some amount of energy (thermal energy) is required to break the bonds and “squeeze” past its neighbors.

- The energy necessary for motion, $\mathbf{Q_d}$, is ***activation energy for diffusion***.

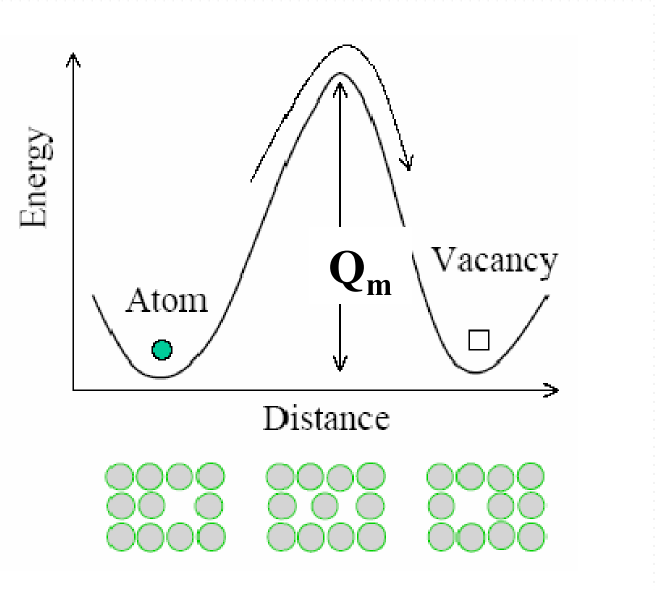
DIFFUSION MECHANISMS: COMPARISON



- Typically, activation energies for vacancy diffusion, q_v, is higher than those for interstitial diffusion, q_i.

- Thus interstitial diffusion occurs ***more rapidly*** than diffusion by vacancies.

Diffusion Coefficient



The average thermal energy of atom is E ~ k_BT (e.g. E=0.026 eV/atom at T=300K) is smaller than the Q_m (~1 eV/atom)

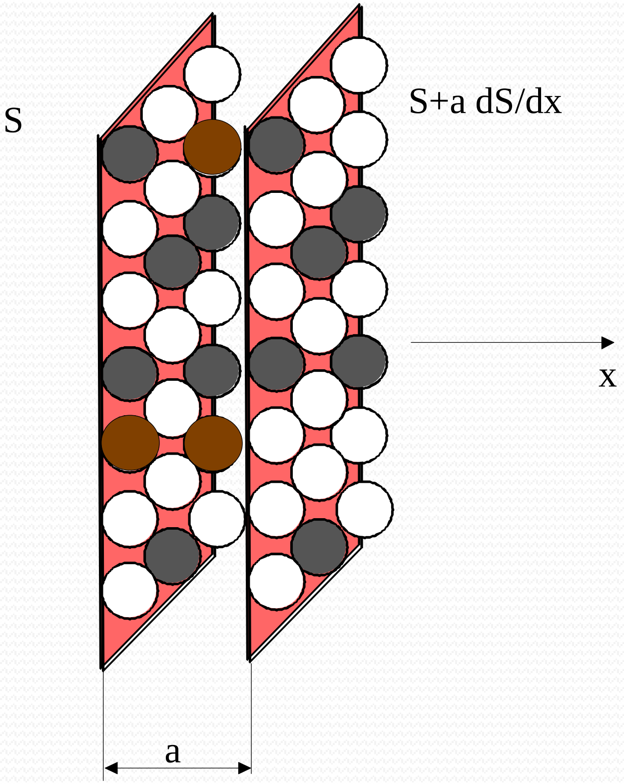
If the energy barrier is of height Q_m , the atom will have sufficient thermal energy to pass over the barrier only a fraction of exp($-Q_m/RT$) of the time.

If ν is a characteristic vibrational atomic frequency, then the probability **p** that during one second atom will have enough thermal energy is:

$\mathbf{p} = \nu \exp(-Q_m/k_BT)$ – ***jump frequency***

Values of ν are of the order $10^{14}\ s^{-1}$

Diffusion Coefficient: Interstitial Mechanism



p = ν $\exp(-Q_m/k_BT)$ – ***jump frequency***

Let us introduce:
a – lattice constant
S – number of impurity atoms on one plane

In this case the net number of atoms, N, crossing between the planes in one second is:

N = - **p**·a·dS/dx

In turn S=a·C, where C – concentration of impurity atoms. Than diffusion flux, J, can be written as follows:

$J = -pa^2(dC/dx)$
Compare with Fick's Law: J = D (dC/dx) one has:

$$\boxed{D = \nu a^2 \exp(-Q_m/k_BT) \text{ and } D_0 = \nu a^2}$$

Diffusion Coefficient: Vacancy Mechanism

In this case in addition to $\mathbf{p} = \nu \exp(-Q_m/k_BT)$ – the probability that during one second atom will have enough thermal energy to overcome the energy barrier for vacancy motion

one has to account, $\mathbf{P}_v = N\exp(-Q_v/RT)$ - the probability of finding a vacancy an adjacent lattice site (see Chapter 4).

In this case diffusion coefficient can be written as follows:

$D = \nu\, a^2\, N \exp((-Q_v/RT)\cdot\exp(-Q_m/k_BT)$ and $D_o = N\, \nu a^2 \exp(-(Q_m+Q_v)/kT)$

$$\boxed{D=D_o\exp\,(-Q_d/kT) \text{ where } D_o= N\,\nu a^2 \text{ and } Q_d=Q_m+Q_v}$$

Factors that Influence Diffusion

- Temperature - diffusion rate increases very rapidly with increasing temperature

- Diffusion mechanism - interstitial is usually faster than vacancy

- Diffusing and host species - Do, Q_d is different for every solute, solvent pair

- Microstructure - diffusion faster in polycrystalline vs. single crystal materials because of the accelerated diffusion along grain boundaries and dislocation cores.

DIFFUSION AND TEMPERATURE

- **Diffusivity increases with T.**

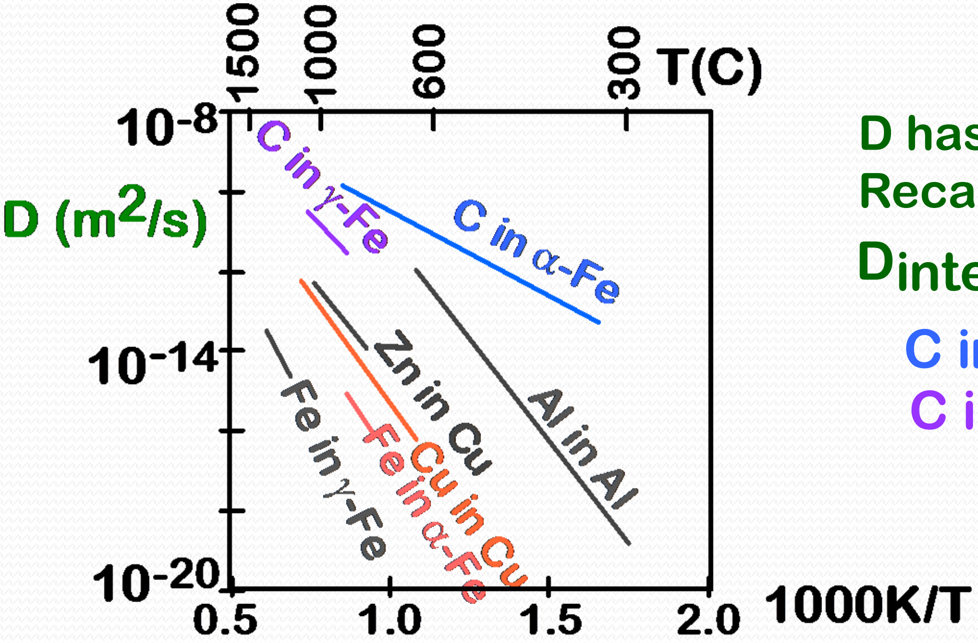
pre-exponential [m²/s]

activation energy

diffusivity $$D = D_o \exp\left(-\frac{Q_d}{RT}\right)$$ [J/mol],[eV/mol]

gas constant [8.31J/mol-K]

- **Experimental Data:**



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

$$D_{interstitial} \gg D_{substitutional}$$

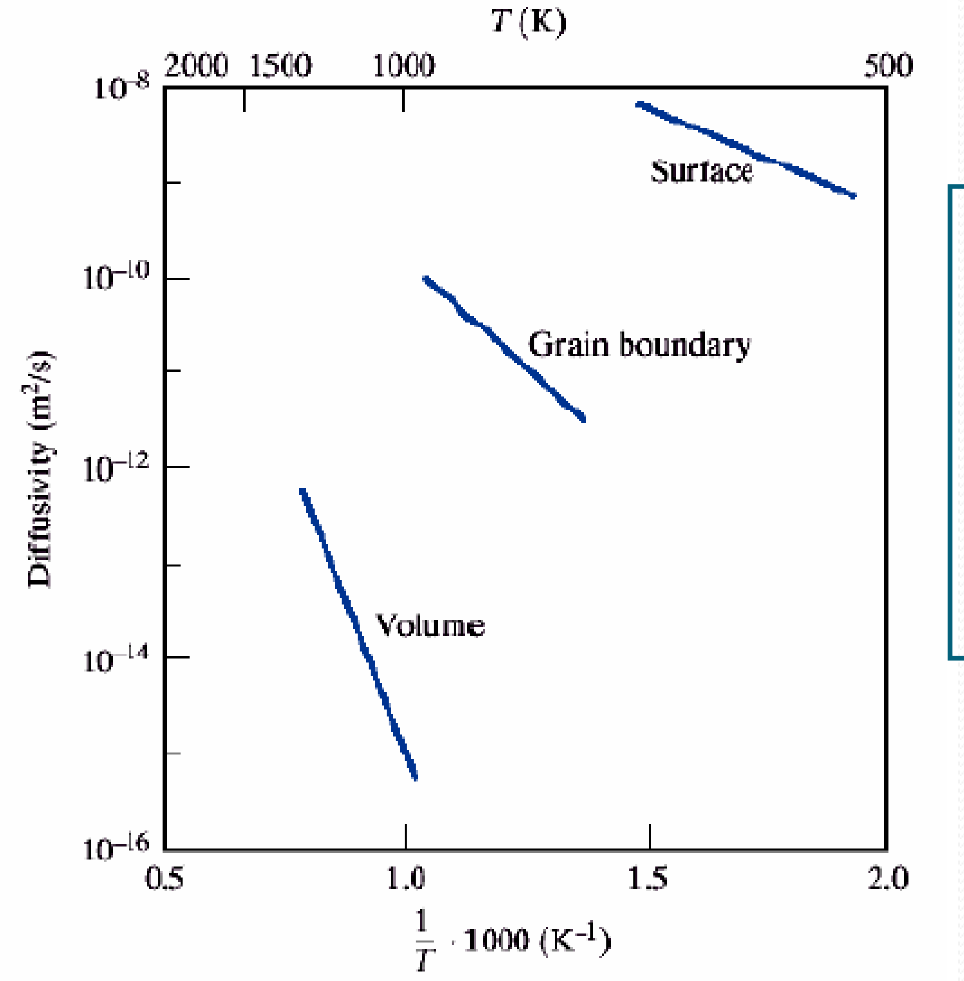
$D_{interstitial}$	$D_{substitutional}$
C in α-Fe	Cu in Cu
C in γ-Fe	Al in Al
	Fe in α-Fe
	Fe in γ-Fe
	Zn in Cu

Diffusion in Polycrystalline Materials

In most solids we are not dealing with single crystals but rather with polycrystalline materials which contain a large number of grain boundaries (internal surfaces). As expected, the rate of diffusion along grain boundaries is much higher than that for volume diffusion ($D_{volume} < D_{g\text{-}boundary}$). FInally, surface diffusion, which takes place on all external surfaces, is even higher ($D_{volume} < D_{g\text{-}boundary} < D_{surface}$). The respective activation energies for diffusion are:

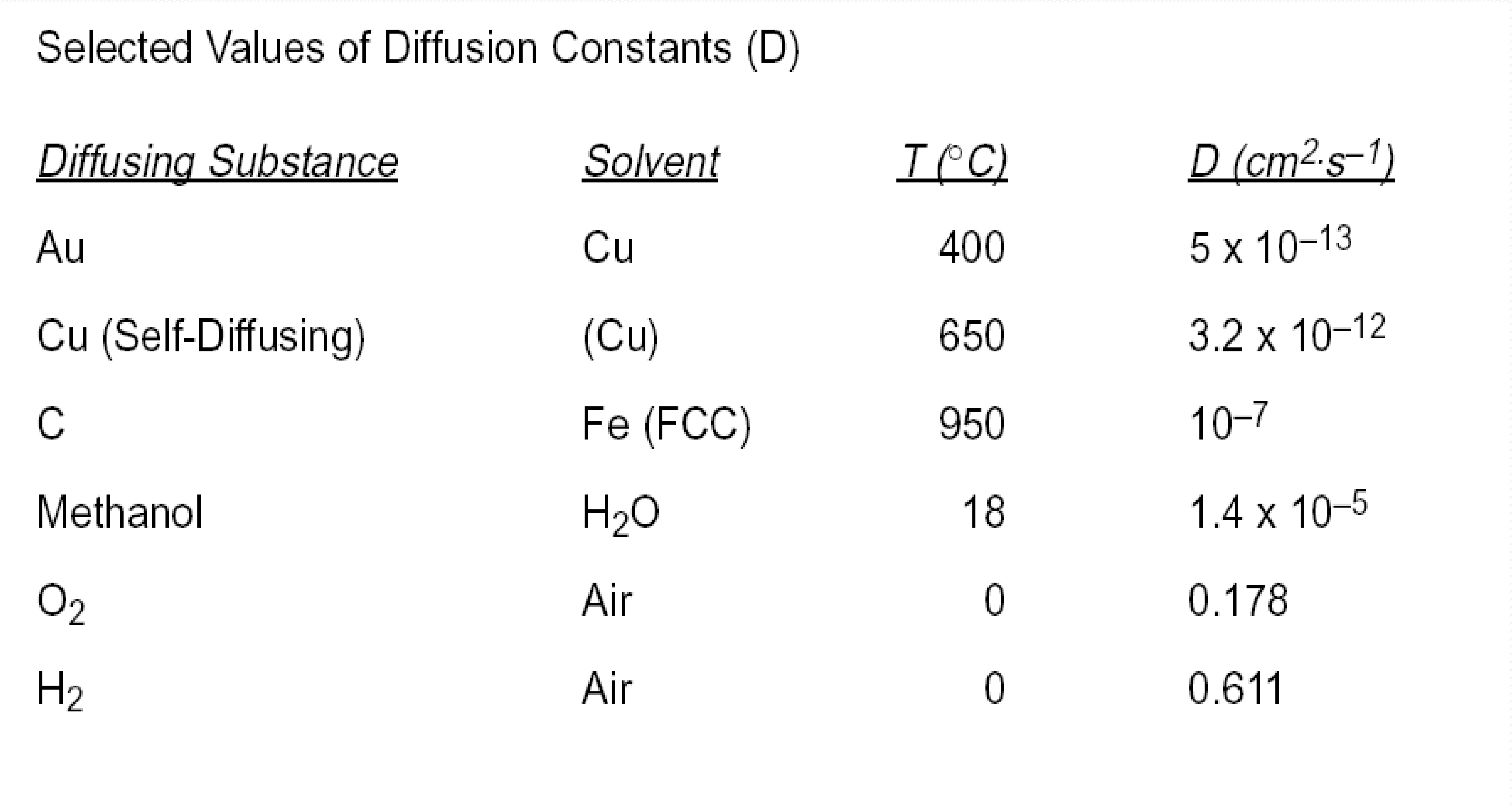
$$E_a \text{ surface} < E_a \text{ grain boundary} < E_a \text{ volume}$$

Microstructure and Diffusion



Self-diffusion coefficients for Ag depend on the diffusion path. In general, diffusion is greater through less restrictive structural regions, i.e., grain boundaries, dislocation cores, external surfaces.

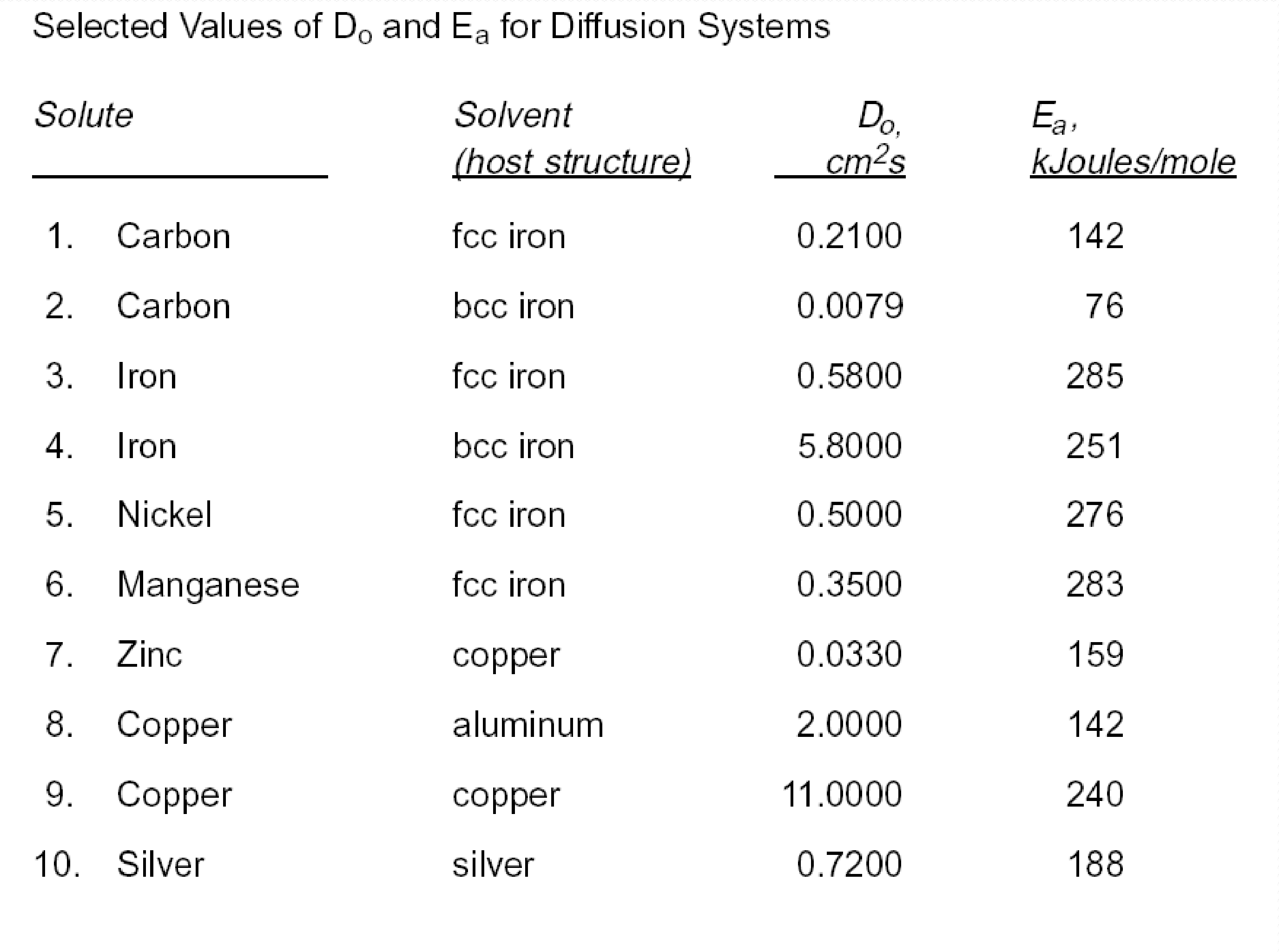
Table 1



Selected Values of Diffusion Constants (D)

Diffusing Substance	*Solvent*	*T (°C)*	*D* ($cm^2 \cdot s^{-1}$)
Au	Cu	400	5×10^{-13}
Cu (Self-Diffusing)	(Cu)	650	3.2×10^{-12}
C	Fe (FCC)	950	10^{-7}
Methanol	H_2O	18	1.4×10^{-5}
O_2	Air	0	0.178
H_2	Air	0	0.611

Table 2



Selected Values of D_o and E_a for Diffusion Systems

	Solute	*Solvent (host structure)*	*D_o, cm^2s*	*E_a, kJoules/mole*
1.	Carbon	fcc iron	0.2100	142
2.	Carbon	bcc iron	0.0079	76
3.	Iron	fcc iron	0.5800	285
4.	Iron	bcc iron	5.8000	251
5.	Nickel	fcc iron	0.5000	276
6.	Manganese	fcc iron	0.3500	283
7.	Zinc	copper	0.0330	159
8.	Copper	aluminum	2.0000	142
9.	Copper	copper	11.0000	240
10.	Silver	silver	0.7200	188

SUMMARY: STRUCTURE & DIFFUSION

Diffusion **FASTER** for...	Diffusion **SLOWER** for...
open crystal structures	close-packed structures
lower melting T materials	higher melting T materials
materials w/secondary bonding	materials w/covalent bonding
smaller diffusing atoms	larger diffusing atoms
cations	anions
lower density materials	higher density materials