

# Diffusion and Fick's law

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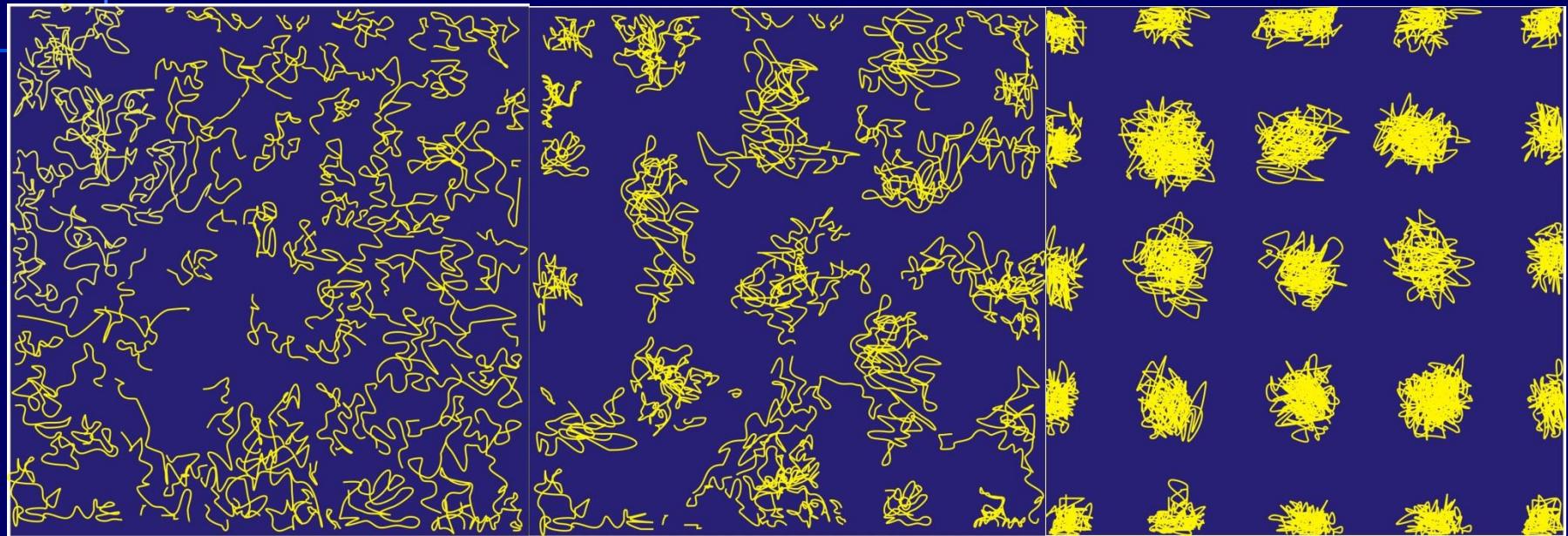
# *Diffusion, flux, and Fick's law*

## **Diffusion:**

- (1) motion of one or more particles of a system relative to other particles (Onsager, 1945)**
- (2) It occurs in all materials at all times at temperatures above the absolute zero**
- (3) The existence of a driving force or concentration gradient is not necessary for diffusion**



# *Diffusion, flux, and Fick's law*



Gas

Liquid

Solid

# Mass Transport Of Solutes



Figure 16-22 Tracing disappearing stream water. (left) Dye is poured into a stream. Colored water emerges several hours later from a natural spring several kilometers downstream.

They all depend on

## **Diffusion (conduction)**

What is diffusion? The transport of material--atoms or molecules--by random motion

What is conduction? The transport of heat or electrons by random motion.



# Diffusion

**Mass transport by atomic motion**

**Mechanisms**

**Gases & Liquids – random (Brownian) motion**

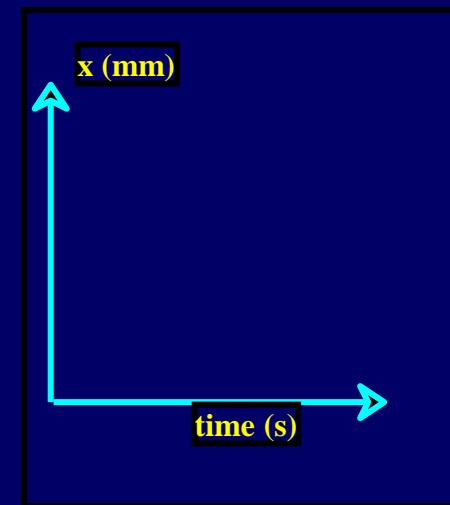
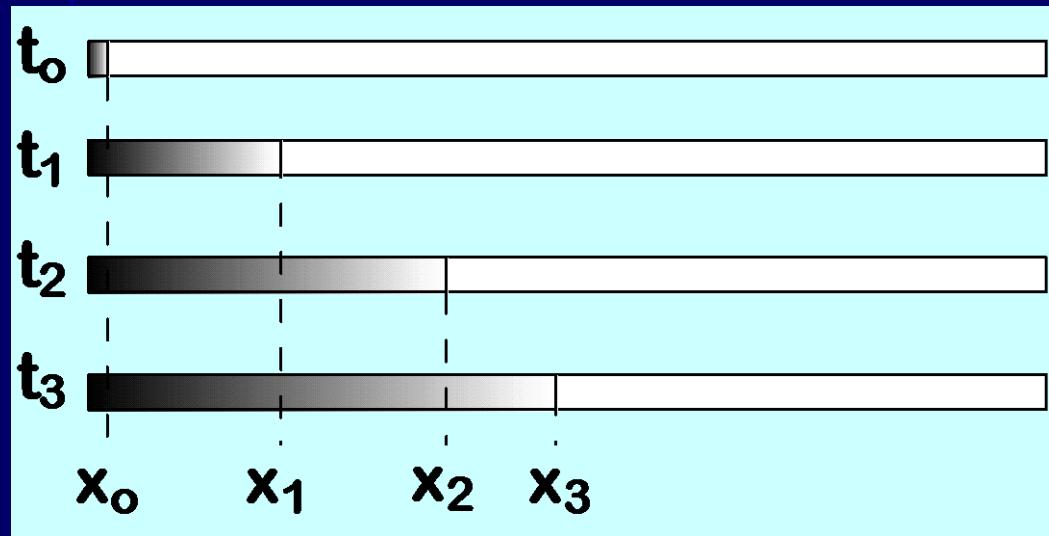
**Solids – vacancy diffusion or interstitial diffusion**

**Cause (Driving force)**  
**Concentration gradient**



# Diffusion: gases and liquids

- 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.



Possible to measure concentration

# Mass Transfer

**Mass transfer occurs when a component in a mixture goes from one point to another.**

**Mass transfer can occur by either diffusion or convection.**

**Diffusion is the mass transfer in a stationary solid or fluid under a concentration gradient.**

**Convection is the mass transfer between a boundary surface and a moving fluid or between relatively immiscible moving fluids.**



# Example of Mass Transfer

Mass transfer can occur by either diffusion or by convection.

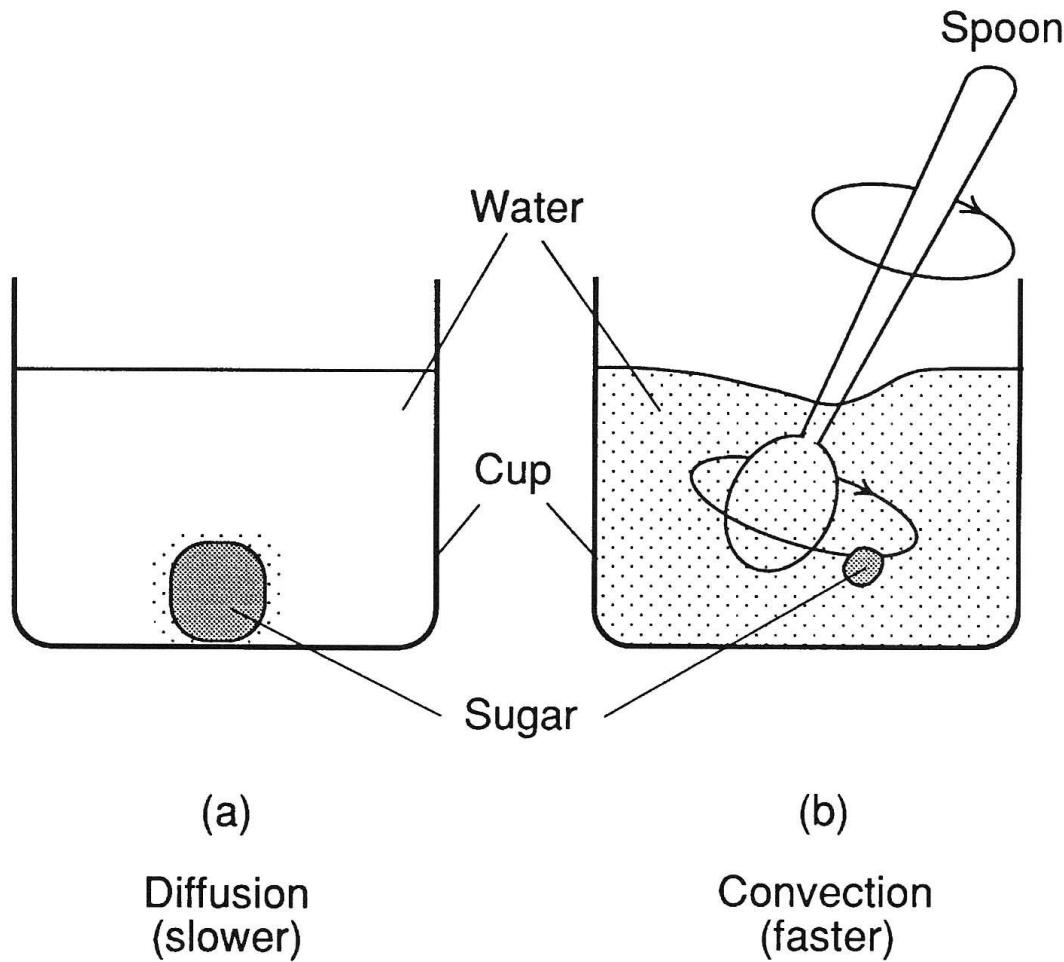


Fig. 3.1-1 Mass transfer mechanisms: (a) diffusion; (b) convection.

Stirring the water with a spoon creates forced convection.

That helps the sugar molecules to transfer to the bulk water much faster.

*After adding milk and sugar, why do we stir our coffee?*

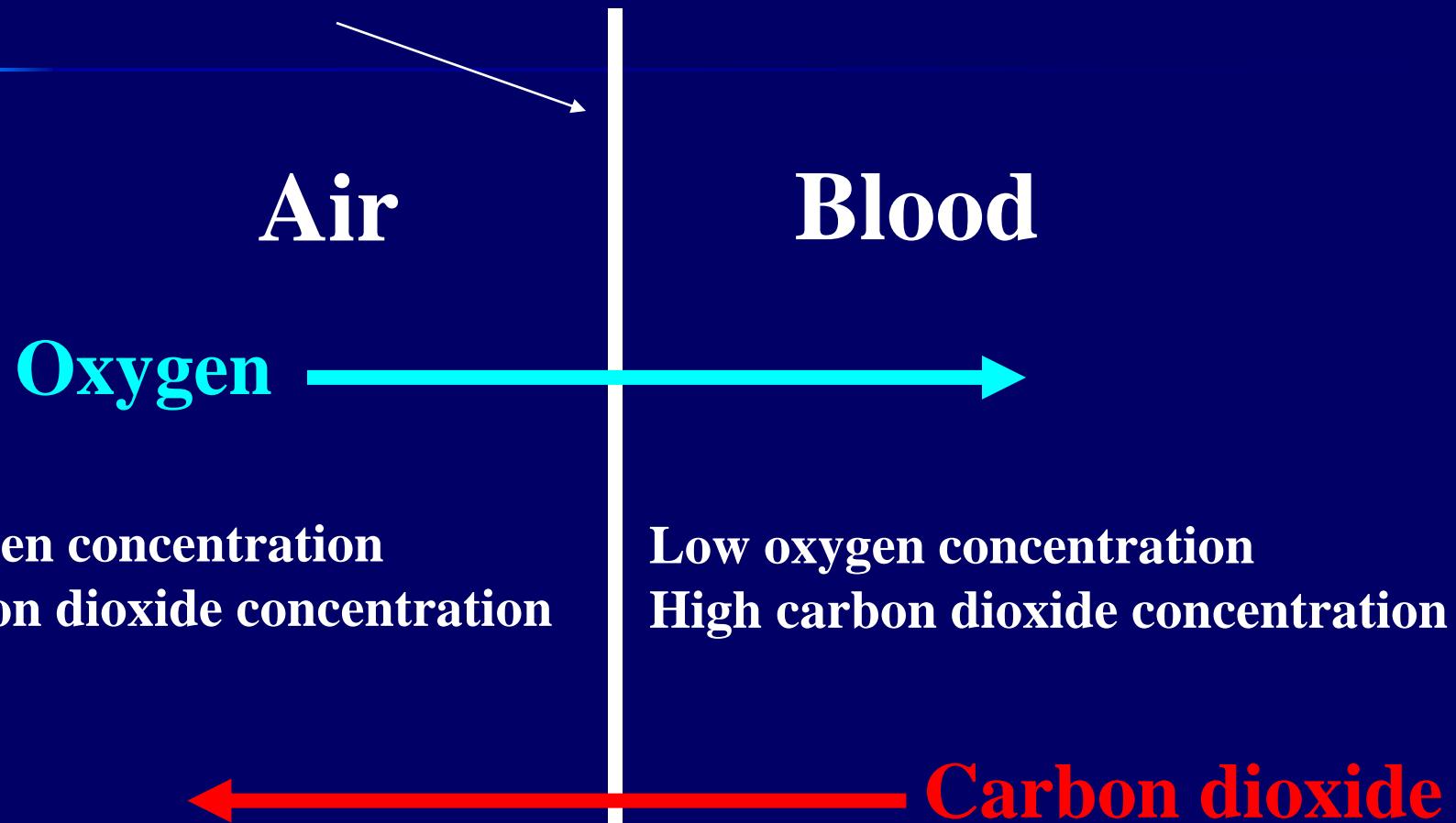


*Diffusion is slow!*

*Agitation (or stirring) can move fluids much larger distances in the same amount of time, which can accelerate the diffusion process.*

# Example of Mass Transfer

At the surface of the lung:



# Diffusion

Diffusion (also known as molecular diffusion) is a net transport of molecules from a region of higher concentration to a region of lower concentration by random molecular motion.



# Diffusion

A

B

Liquids A and B are separated from each other.

A

B

A goes from high concentration of A to low concentration of A.

B goes from high concentration of B to low concentration of B.

Molecules of A and B are uniformly distributed everywhere in the vessel purely due to the DIFFUSION.

*Place a drop of ink into a glass of water. What happens?*

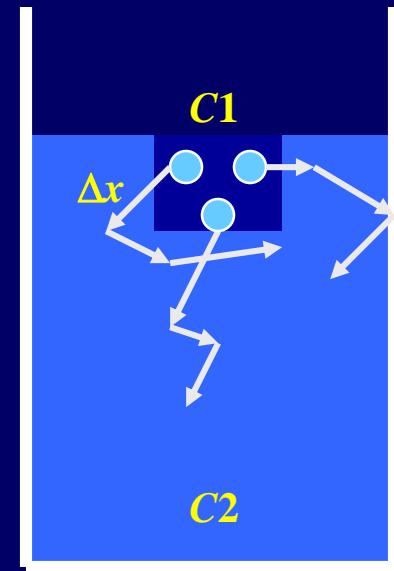


**Brownian motion causes the ink particles to move erratically in all directions. A concentration of ink particles will disperse.**

# Concentrated Region

- Molecules in a concentrated region will disperse into the rest of the medium.
- The difference in concentrations is the concentration gradient.

$$\frac{-\Delta C}{\Delta x} = \frac{C_1 - C_2}{\Delta x}$$



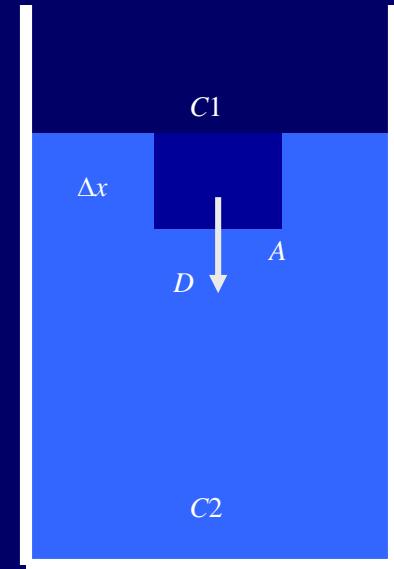
# Diffusion Constant

- **Different materials pass through an area at different rates.**
  - Depends on concentrate
  - Depends on medium

$O_2$  in air:  $D = 1.8 \times 10^{-5} \text{ m}^2/\text{s}$

$O_2$  in water:  $D = 1.0 \times 10^{-9} \text{ m}^2/\text{s}$

DNA in water:  $D = 1.3 \times 10^{-12} \text{ m}^2/\text{s}$



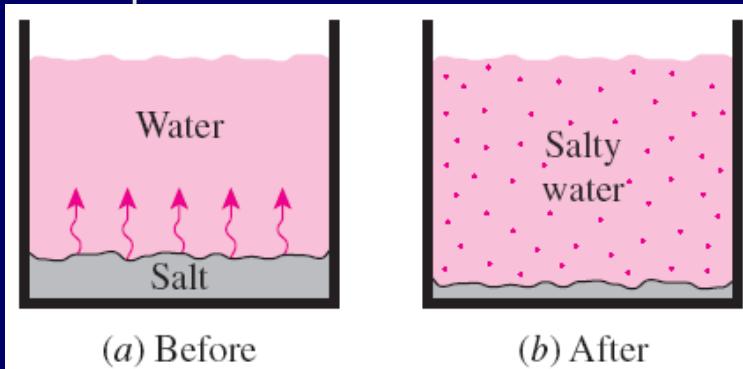
# *Values for Diffusivity D*

		Temperature (°C)	Diffusivity (cm <sup>2</sup> /s)
(gas)	CO <sub>2</sub> -N <sub>2</sub> 0	0	0.096
	Ar-O <sub>2</sub>	20	0.2
(liquid)	Ethanol(5%)-Water	25	1.13E-05
	Water(13%)-Butanol	30	1.24E-05
(solid)	H <sub>2</sub> -Ni	85	1.16E-08
	Al-Cu	20	1.30E-30

*Greater the diffusivity, greater the flux!*

# Diffusion & Transport

Whenever there is an imbalance of a commodity in a medium, nature tends to redistribute it until a “balance” or “equality” is established. This tendency is often referred to as the *driving force*, which is the mechanism behind many naturally occurring transport phenomena.



**FIGURE 14-1**

Whenever there is concentration difference of a physical quantity in a medium, nature tends to equalize things by forcing a flow from the high to the low concentration region.

The commodity simply creeps away during redistribution, and thus the flow is a *diffusion process*. The rate of flow of the commodity is proportional to the *concentration gradient*  $dC/dx$ , which is the change in the concentration  $C$  per unit length in the flow direction  $x$ , and the area  $A$  normal to flow direction.

$$\text{Flow rate} \propto (\text{Normal area})(\text{Concentration gradient})$$

$$\dot{Q} = -k_{\text{diff}} A \frac{dC}{dx}$$

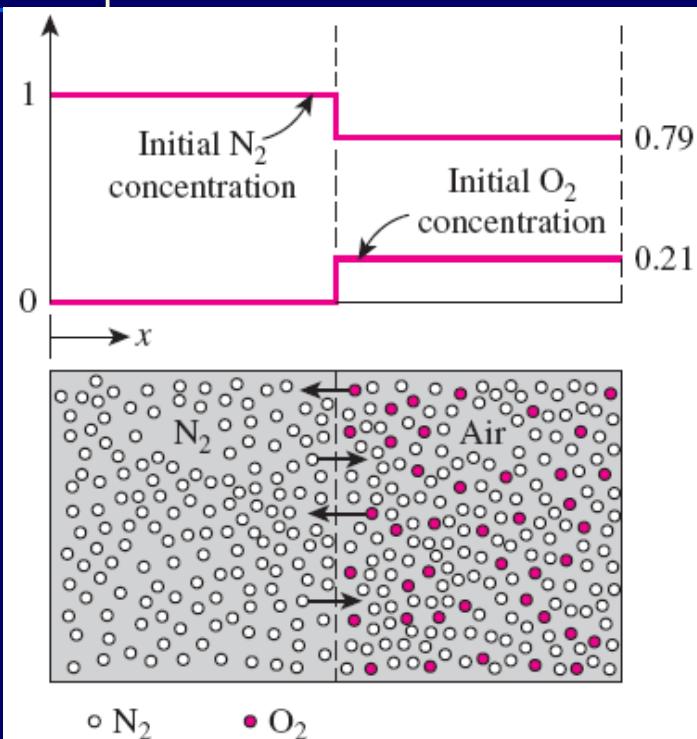
$k_{\text{diff}}$  is the *diffusion coefficient* of the medium, which is a measure of how fast a commodity diffuses in the medium, and the negative sign is to make the flow in the positive direction a positive quantity (note that  $dC/dx$  is a negative quantity since concentration decreases in the flow direction).

The diffusion coefficients and thus diffusion rates of gases depend strongly on temperature.

The diffusion rates are higher at higher temperatures.

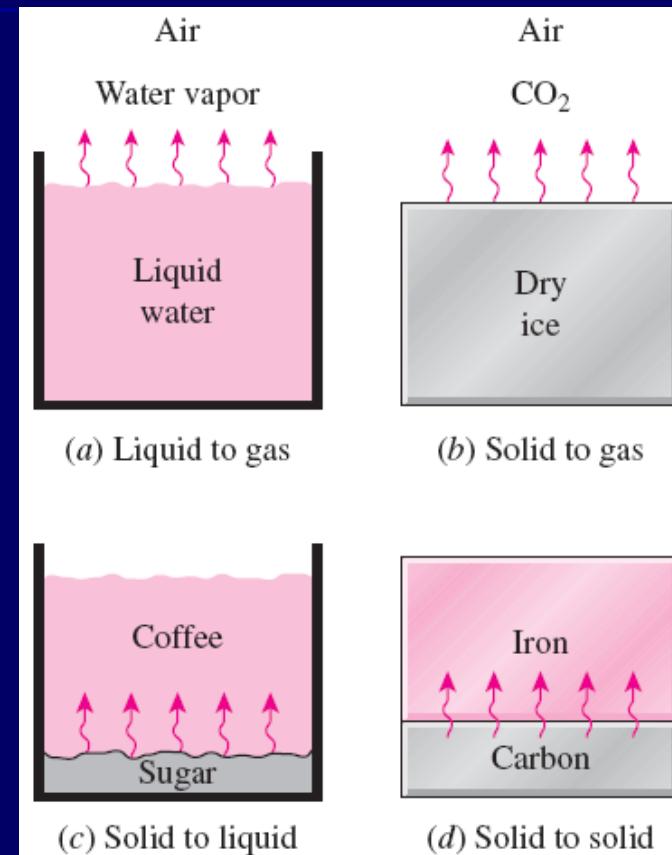
The larger the *molecular spacing*, the higher the diffusion rate.

Diffusion rate: gases > liquids > solids



**FIGURE 14-2**

A tank that contains N<sub>2</sub> and air in its two compartments, and the diffusion of N<sub>2</sub> into the air (and the diffusion of O<sub>2</sub> into N<sub>2</sub>) when the partition is removed.



**FIGURE 14-3**  
Some examples of mass transfer that involve a liquid and/or a solid.

# Analogy Between Heat And Mass Transfer

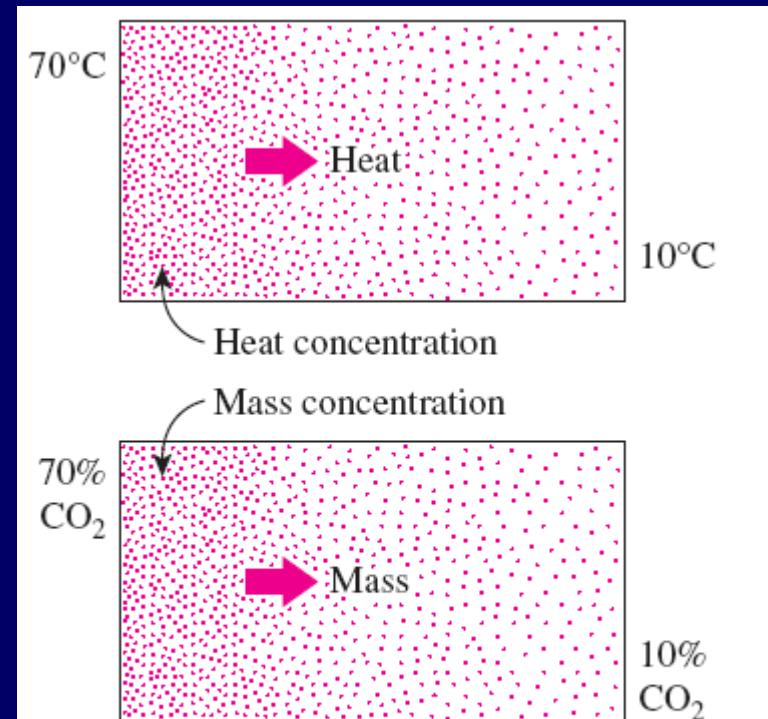
We can develop an understanding of mass transfer in a short time with little effort by simply drawing *parallels* between heat and mass transfer.

## Temperature

The driving force for mass transfer is the *concentration difference*.

Both heat and mass are transferred from the more concentrated regions to the less concentrated ones.

If there is no difference between the concentrations of a species at different parts of a medium, there will be no mass transfer.



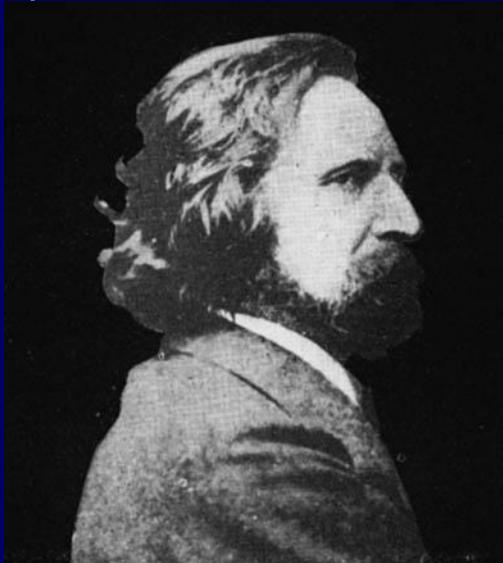
**FIGURE 14-4**  
Analogy between heat and mass transfer.

# Fick's Law

Gradient

$$\nabla = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

During diffusion we assume particles move in the direction of least density. They move down the concentration gradient



**Adolph Fick**

**Born: 1829**

**Cassel, Germany**

**Died: 1879**

In mathematical terms we will assume

$$\vec{J} = -D \nabla u$$

Where D is a constant of proportionality called the Diffusion Coefficient

# Fick's Law

- The rate of diffusion depends on the concentration gradient, area (A) , and diffusion constant (D).

$$J = DA \frac{C_1 - C_2}{\Delta t}$$

- $J$  measures mol/m<sup>3</sup>.
- There is a diffusion time  $t$  for diffusion in one direction over a distance  $Dx$ .

$$t = \frac{\Delta x^2}{2D}$$

*In each of these examples, molecules (or heat) are moving down a gradient!*

*(From an area of high concentration to an area of low concentration)*

Fick's Law:

$$J_i = -D \frac{dc_i}{dz}$$

J<sub>i</sub> is called the flux. It has units of

$$\frac{\text{amount of material diffused}}{(l^2)(t)}$$

D is called the diffusion coefficient. It has units of

$$\frac{l^2}{t}$$

Mass is transferred by *conduction* (called diffusion) and *convection* only.

$$\dot{Q}_{\text{cond}} = -kA \frac{dT}{dx}$$

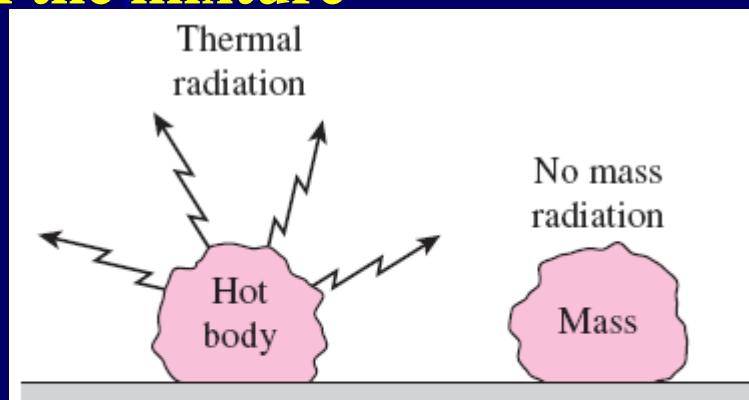
**Rate of mass diffusion**

$$\dot{m}_{\text{diff}} = -D_{AB}A \frac{dC_A}{dx}$$

**Fick's law of diffusion**

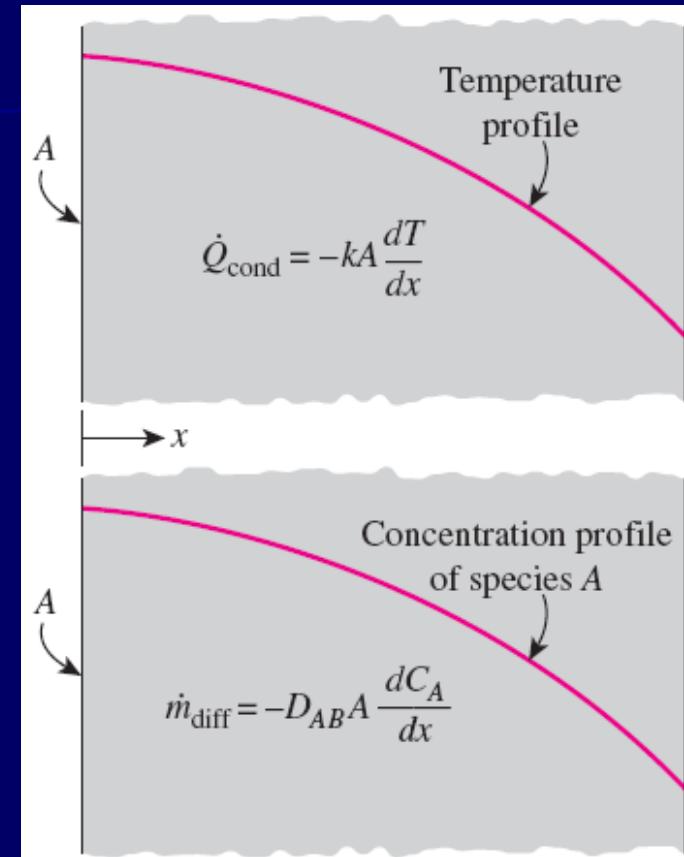
$D_{AB}$  is the diffusion coefficient (or *mass diffusivity*) of the species in the mixture

$C_A$  is the concentration of the species in the mixture



**FIGURE 14–5**

Unlike heat radiation, there is no such thing as mass radiation.



**FIGURE 14–6**

Analogy between heat conduction and mass diffusion.

## What do mass transfer processes have in common?

- 1) Hydrogen embrittlement of pressure vessels in nuclear power plants
- 2) Flow of electrons through conductors
- 3) Dispersion of pollutants from smoke stacks
- 4) Transdermal drug delivery
- 5) Influenza epidemics
- 6) Chemical reactions
- 7) Absorption of oxygen into the bloodstream

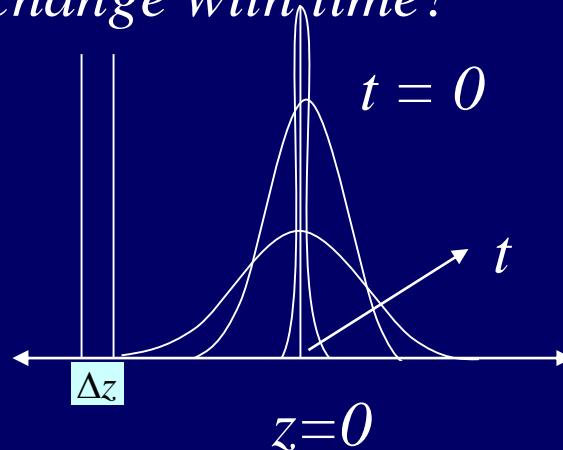


# Unsteady state diffusion

Back to a drop of ink in a glass of water...



If consider diffusion in the z-direction only:  
*How does the concentration profile change with time?*



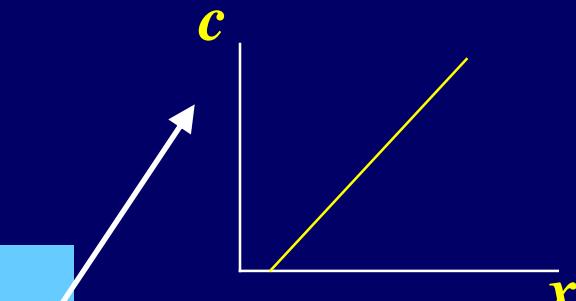
(add ink drop – all ink located at  $z = 0$ )

A measure of the spread due to diffusion is the diffusion length  $L_d = (4Dt)^{0.5}$ , where D is the diffusivity coefficient and t is time. Note: for small time, spreading is quick, but for long times it slows down. That's why you stir your coffee after adding cream. Diffusion doesn't work fast enough over long distances.

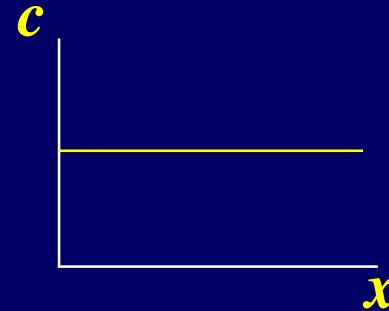
# Fick's first law

$$J = -D \frac{dc}{dx}$$

$D$  = diffusion coefficient



$$J = -D \frac{dc}{dx} < 0$$

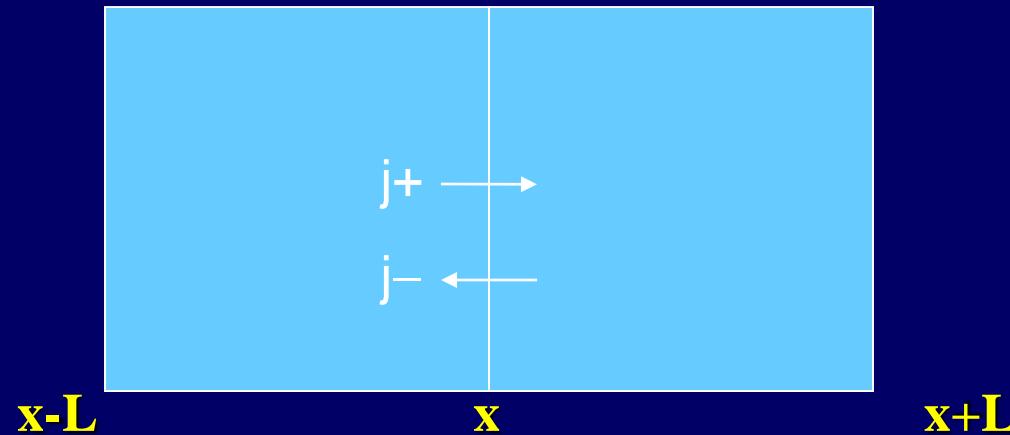


$$J = -D \frac{dc}{dx} = 0$$

# Continuum description of diffusion

We need to derive a differential equation for this purpose.

Divide a box of particles into small cubic bins of size  $L$



$j$ : flux of particles (number of particles per unit area per unit time)

$c$ : concentration of particles (number of particles per unit volume)

Random walk in 1D; half of particles in each bin move to the left and half to the right.

**Right, left and total fluxes at x are given by**

$$j_+ = \frac{\frac{1}{2}c(x - L/2)AL}{A\Delta t}, \quad j_- = \frac{\frac{1}{2}c(x + L/2)AL}{A\Delta t}$$

$$j = j_+ - j_- = \frac{L}{2\Delta t} [c(x - L/2) - c(x + L/2)]$$

**Taylor expanding the concentrations for small L gives**

$$j = \frac{L}{2\Delta t} \left[ c(x) - \frac{L}{2} \frac{dc}{dx} + \dots - \left( c(x) + \frac{L}{2} \frac{dc}{dx} + \dots \right) \right]$$

$$= -\frac{L^2}{2\Delta t} \frac{dc}{dx} = -D \frac{dc}{dx}, \quad \text{Fick's law}$$

**Generalise to 3D:**  $\mathbf{j} = -D \nabla c$

**Flux direction:** particles move from high concentration to low concentration

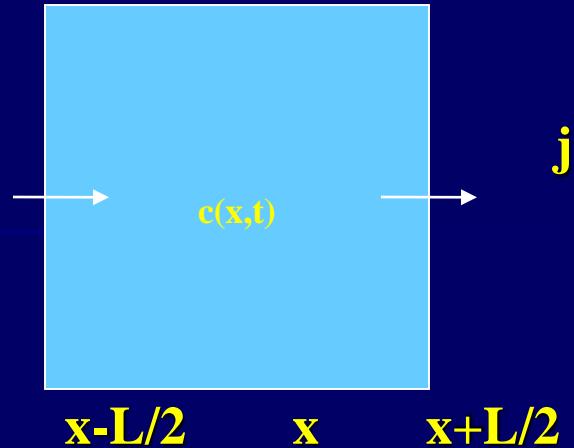


## Conservation laws:

Total number of particles is conserved.

If there is a net flow of particles inside a bin,

the concentration inside must increase by  
the same amount.



$$[c(x, t + \Delta t) - c(x, t)]AL = [j(x - L/2) - j(x + L/2)]A\Delta t$$

$$\frac{\Delta c}{\Delta t}L = j(x) - \frac{L}{2}\frac{dj}{dx} + \dots - \left( j(x) + \frac{L}{2}\frac{dj}{dx} + \dots \right)$$

$$\frac{dc}{dt} = -\frac{dj}{dx}$$

$$\frac{dc}{dt} = -\nabla \cdot \mathbf{j}$$

Generalise to 3D:

(similar to charge conservation)

Integrate the conservation equation over a closed volume V with N part's

$$\int_V \frac{dc}{dt} dV = - \int_V \nabla \cdot \mathbf{j} dV$$

$$\frac{d}{dt} \int_V c dV = - \oint_S \mathbf{j} \cdot \mathbf{n} da$$

$$\frac{dN}{dt} = -\Phi$$

(Divergence theorem)

(rate of change of N = - total flux out)

We can use the conservation equation to eliminate flux from Fick's eq'n.

$$j = -D \frac{dc}{dx}, \quad \rightarrow \quad \frac{dj}{dx} = -D \frac{d^2c}{dx^2} \quad \rightarrow \quad \frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

Fick's 2<sup>nd</sup> law  
Diffusion eq.

Generalise to 3D:

$$\frac{dc}{dt} = D \nabla^2 c$$

(analogy with the Schroedinger Eq.)

Once the initial conditions are specified, the diffusion equation can be solved numerically using a computer.

### Special cases:

1. **Equilibrium:**  $c(x) = \text{const.} \rightarrow j = 0$ ,  $c$  is uniform and constant
2. **Steady-state diffusion:**  $c(x) = c_0$  for  $x < 0$  and  $c(x) = c_L$  for  $x > L$

**No time dependence,**  $\frac{dc}{dt} = 0, \rightarrow \frac{dj}{dx} = 0, \therefore j = \text{const.}$

$$j = -D \frac{dc}{dx}, \rightarrow c = -\frac{j}{D}x + b$$

$$c_0 = b, \quad c_L = -\frac{j}{D}L + c_0 \quad \rightarrow \quad j = -D \frac{c_L - c_0}{L}$$

$$c = \frac{c_L - c_0}{L} x + c_0 \quad \text{for } 0 < x < L$$

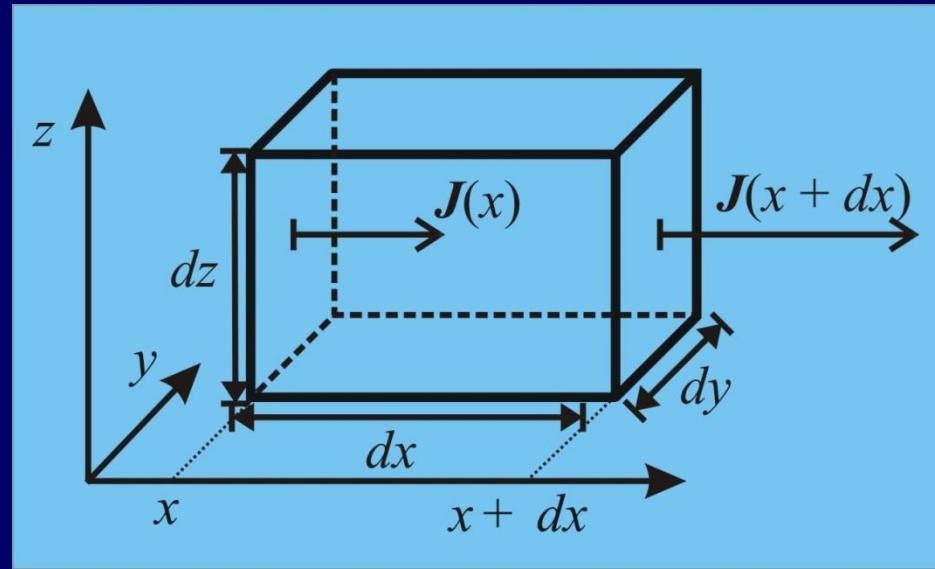


# *Diffusion, flux, and Fick's law*

Fick's second law: mass balance of fluxes

Analogy: gain or loss in your bank account per month =

Your salary (\$\$ per month) - what you spend (\$\$ per month)



$$\frac{\partial C(x, t)}{\partial t} = - \frac{\partial J}{\partial x}$$

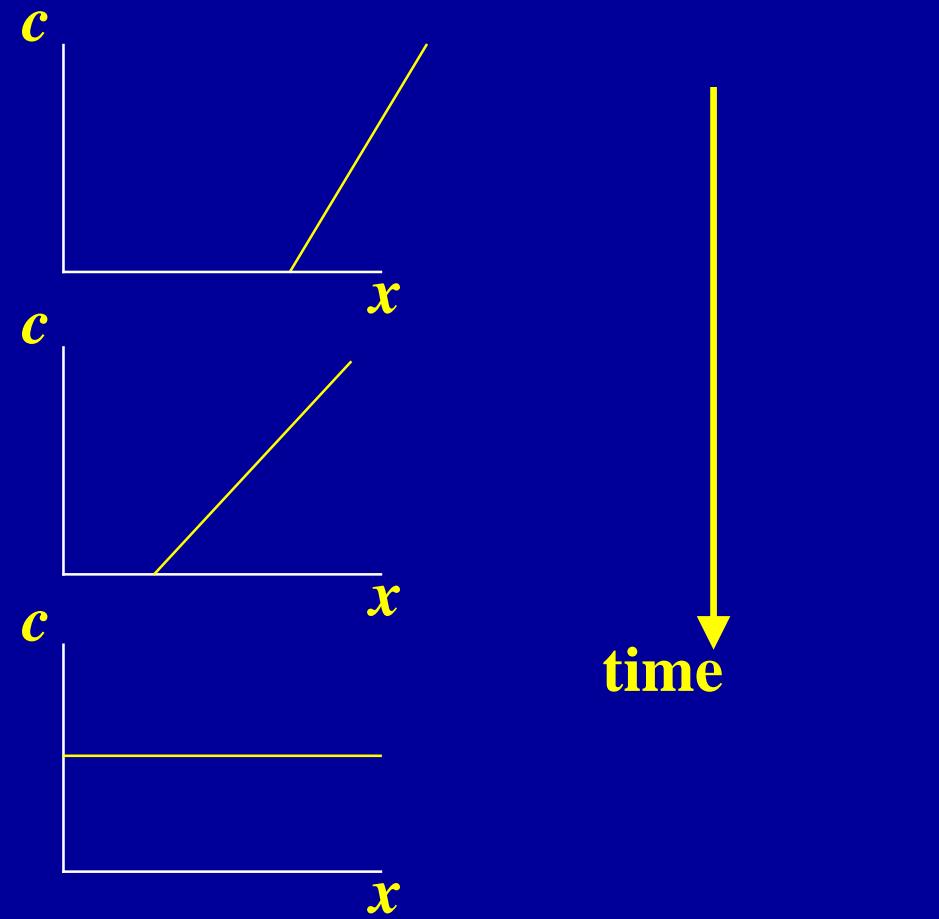
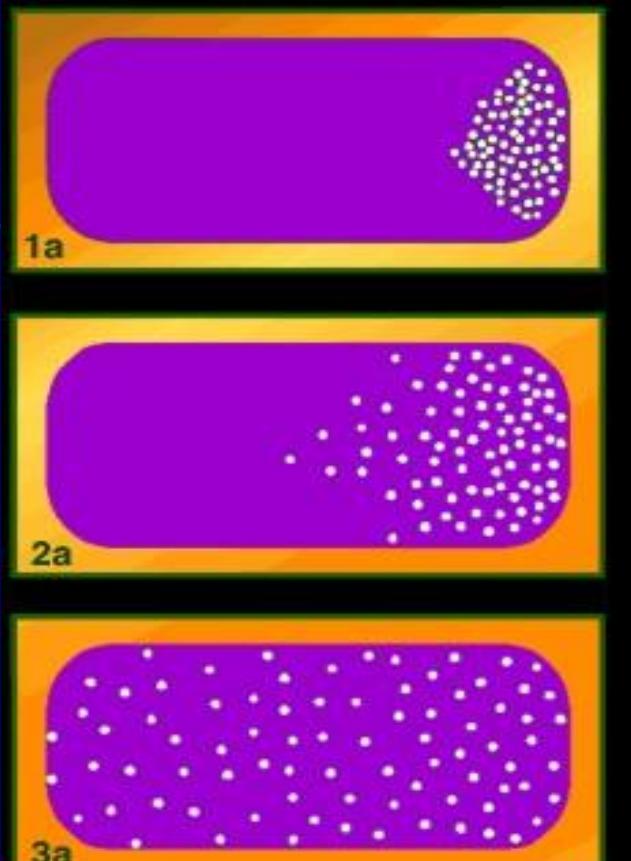
$$\frac{\partial C(x, t)}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C(x, t)}{\partial x} \right)$$

# *Diffusion, flux, and Fick's law*

## Fick's second law: mass balance of fluxes

1. We need to solve the partial differential diffusion equation. (a) analytical solution (e.g., Crank, 1975) or (b) numerical methods
2. We need to know initial and boundary conditions. This is straightforward for ‘exercise cases’, less so in nature.
3. We need to know the diffusion coefficient

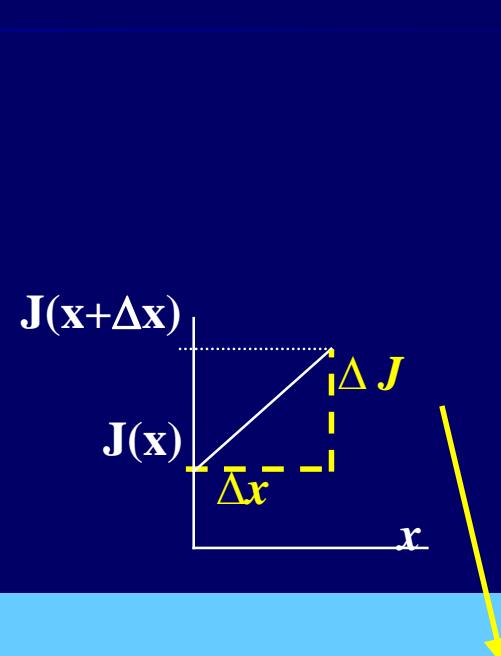
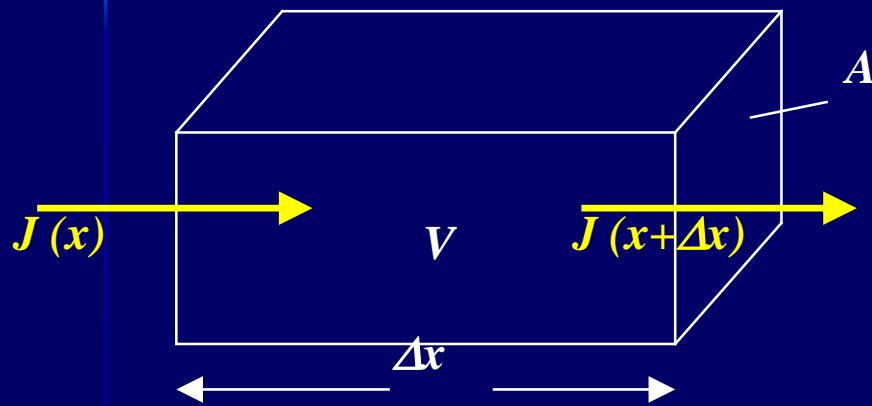




How can we find out  $c(x,t)$  ?

# $N = \text{number of particles in volume } V$

Flux in 1 dimension:



$$\frac{\Delta N}{\Delta t} = J(x)A - J(x + \Delta x)A = -A[J(x + \Delta x) - J(x)] = -A \Delta J \approx$$

$$\approx -A \frac{dJ}{dx} \Delta x = -V \frac{dJ}{dx} \rightarrow \frac{dc}{dt} = \frac{d(N/V)}{dt} = -\frac{dJ}{dx}$$

# How can we find out $c(x,t)$ ?

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

$$J = -D \frac{dc}{dx}$$

Fick's law

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$



We can find out  $c(x,t)$  !  
Fick's second law

# Fick's Laws

- Combining the continuity equation with the first law, we obtain Fick's second law:

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



- Solutions to Fick's Laws depend on the boundary conditions.
  
- Assumptions
  - D is independent of concentration
  - Semiconductor is a semi-infinite slab with either
    - Continuous supply of impurities that can move into wafer
    - Fixed supply of impurities that can be depleted



# Solutions To Fick's Second Law

- The simplest solution is at steady state and there is no variation of the concentration with time
  - Concentration of diffusing impurities is linear over distance
- This was the solution for the flow of oxygen from the surface to the Si/SiO<sub>2</sub> interface.

$$D \frac{\partial^2 c}{\partial x^2} = 0$$

$$c(x) = a + bx$$



# Solutions To Fick's Second Law

- For a semi-infinite slab with a constant (infinite) supply of atoms at the surface

$$c(x, t) = c_o \operatorname{erfc} \left( \frac{x}{2\sqrt{Dt}} \right)$$

- The dose is

$$Q \equiv \int_0^{\infty} c(x, t) dx = 2c_o \sqrt{Dt/\pi}$$



# Solutions To Fick's Second Law

- Complimentary error function (erfc) is defined as  
 $\text{erfc}(x) = 1 - \text{erf}(x)$
- The error function is defined as

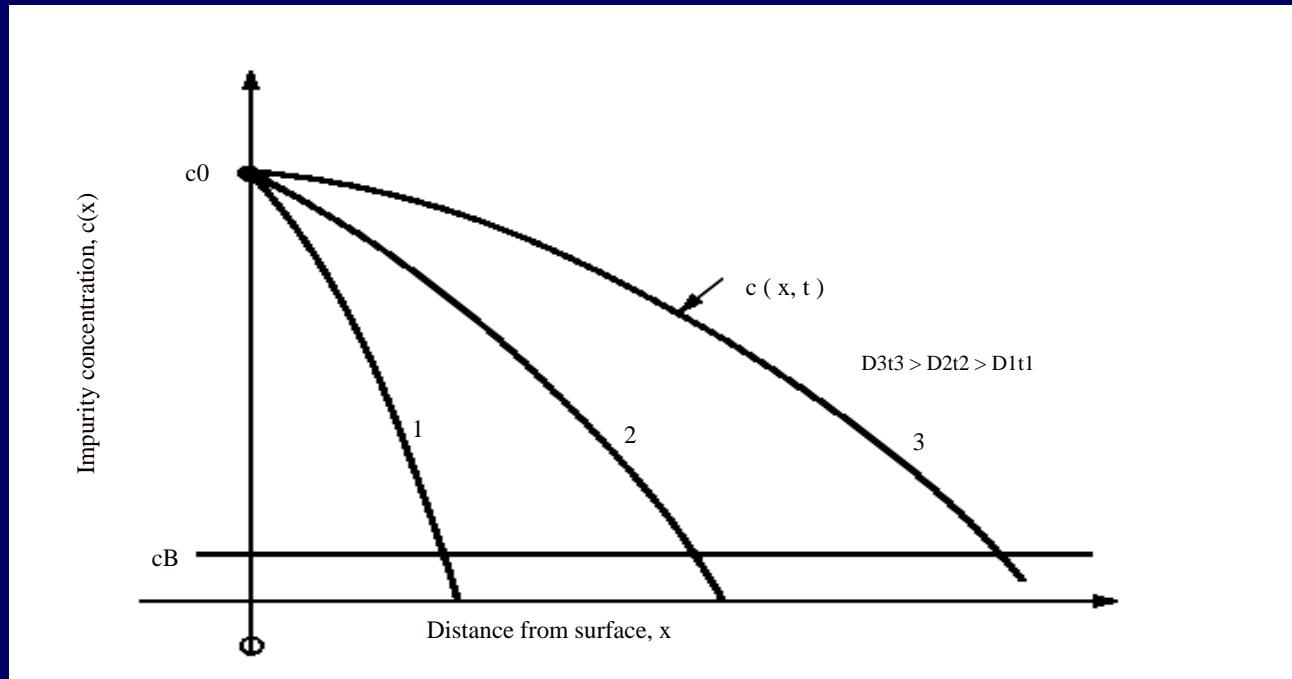
$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\eta^2) d\eta$$

- This is a tabulated function. There are several approximations. It can be found as a built-in function in MatLab, MathCad, and Mathematica



# Solutions To Fick's Second Law

- This solution models short diffusions from a gas-phase or liquid phase source
- Typical solutions have the following shape



# Solutions To Fick's Second Law

- Constant source diffusion has a solution of the form

$$c(x, t) = \frac{Q}{\sqrt{\pi D t}} e^{\frac{-x^2}{4 D t}}$$

- Here, Q is the dose or the total number of dopant atoms diffused into the Si

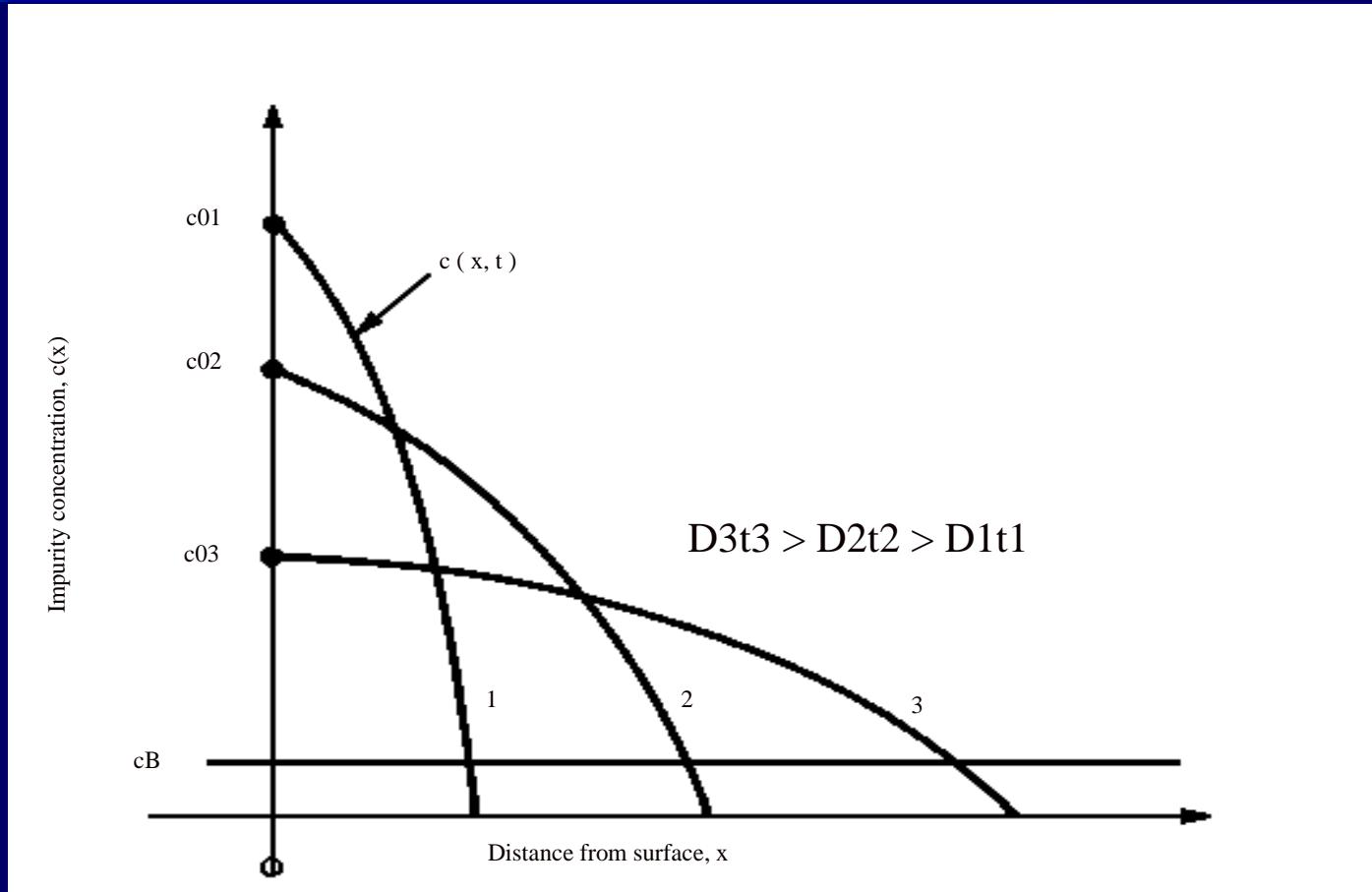
$$Q = \int_0^\infty c(x, t) dx$$

- The surface concentration is given by:

$$c(0, t) = \frac{Q}{\sqrt{\pi D t}}$$

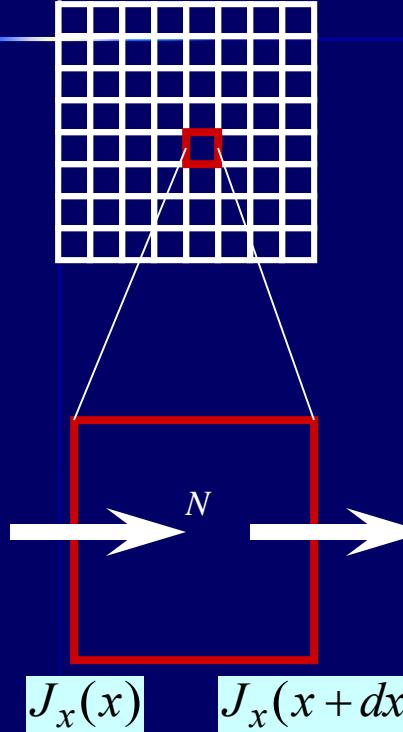
# Solutions To Fick's Second Law

## ■ Limited source diffusion looks like



# Fick's Second Law: The Diffusion Equation

- Consider a small region of space (volume for 3D, area for 2D)



- $J_x(x)$  molecules flow in and  $J_x(x+dx)$  molecules flow out (per unit area or distance per unit time).

$$\left( \frac{\partial N}{\partial t} \right) = (J_x(x) - J_x(x + dx))dy$$

$$\left( \frac{\partial c}{\partial t} \right) = \frac{J_x(x) - J_x(x + dx)}{dx}$$

$$= - \left( \frac{\partial J_x}{\partial x} \right)$$

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

since  $c = N/(dxdy)$

definition of the derivative

$$\text{since } J_x = -D \left( \frac{\partial c}{\partial x} \right)$$

- Flux in 1 dimension:

$$\frac{dc}{dt} = D \frac{d^2 c}{dx^2}$$

- Flux in 2 dimensions:

$$\frac{dc}{dt} = D \left( \frac{d^2 c}{dx^2} + \frac{d^2 c}{dy^2} \right)$$

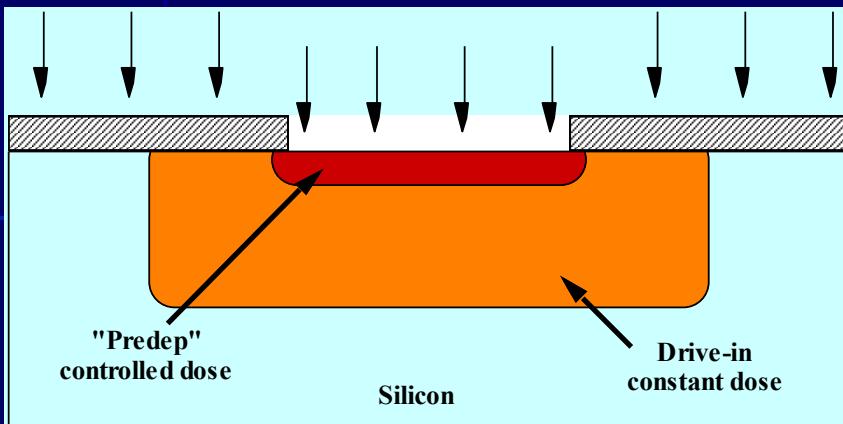
If there is a chemical reaction:

$$F = \frac{\text{number of particles produced}}{\text{volume} \cdot \text{time}}$$

$$\frac{dc}{dt} = F + D \left( \frac{d^2 c}{dx^2} + \frac{d^2 c}{dy^2} \right)$$

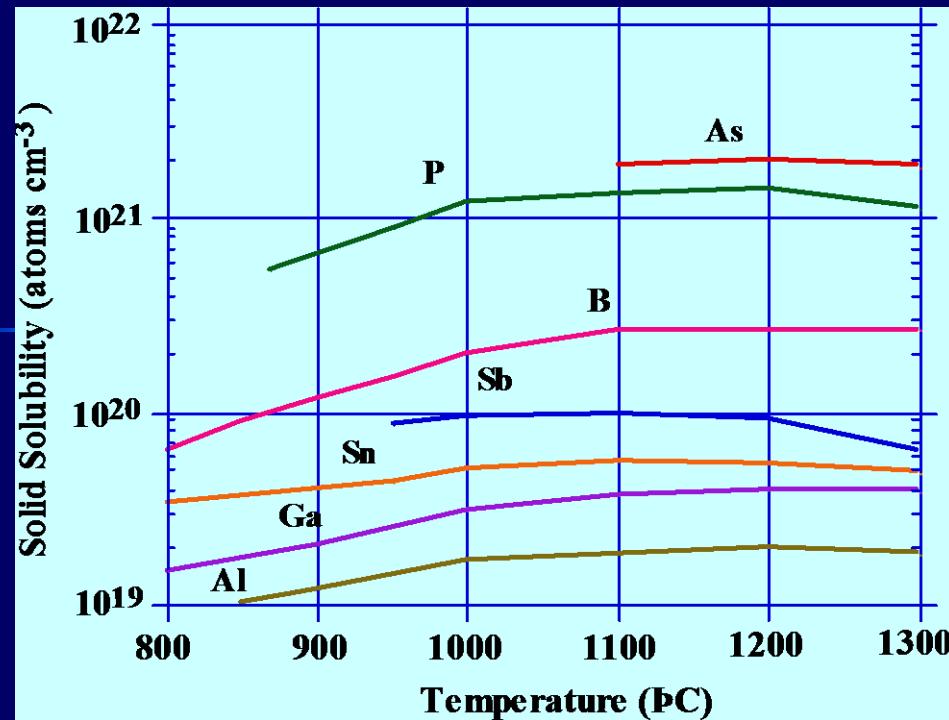
For biological populations:

$$\frac{dp}{dt} = F(p) + D \left( \frac{d^2 p}{dx^2} + \frac{d^2 p}{dy^2} \right)$$

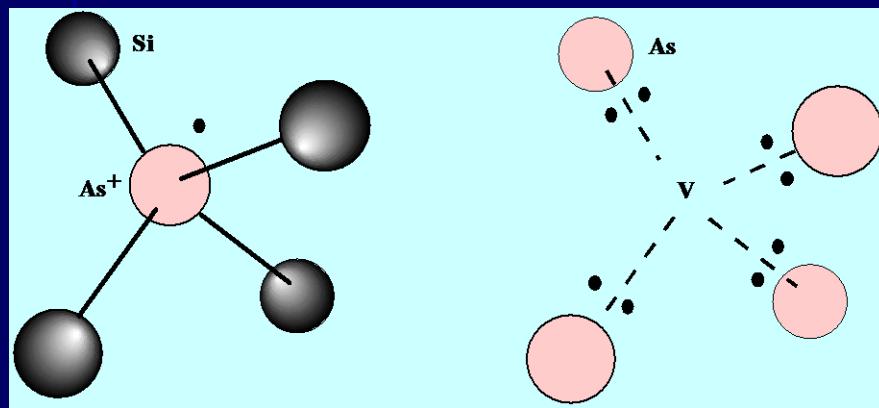


- Diffusion is the redistribution of atoms from regions of high concentration of mobile species to regions of low concentration. It occurs at all temperatures, but the diffusivity has an exponential dependence on T.
- Predeposition: doping often proceeds by an initial predep step to introduce the required dose of dopant into the substrate.
- Drive-In: a subsequent drive-in anneal then redistributes the dopant giving the required  $x_J$  and surface concentration.

	Ion Implantation and Annealing	Solid/Gas Phase Diffusion
Advantages	Room temperature mask Precise dose control $10^{11} - 10^{16}$ atoms $\text{cm}^{-2}$ doses Accurate depth control	No damage created by doping Batch fabrication
Problems	Implant damage enhances diffusion Dislocations caused by damage may cause junction leakage Implant channeling may affect profile	Usually limited to solid solubility Low surface concentration hard to achieve without a long drive-in Low dose predeps very difficult



- Dopants are soluble in bulk silicon up to a maximum value before they precipitate into another phase.



- Dopants may have an “electrical” solubility that is different than the solid solubility defined above.
- One example -  $\text{As}_4\text{V}$  - electrically inactive complex.

# Types of diffusion

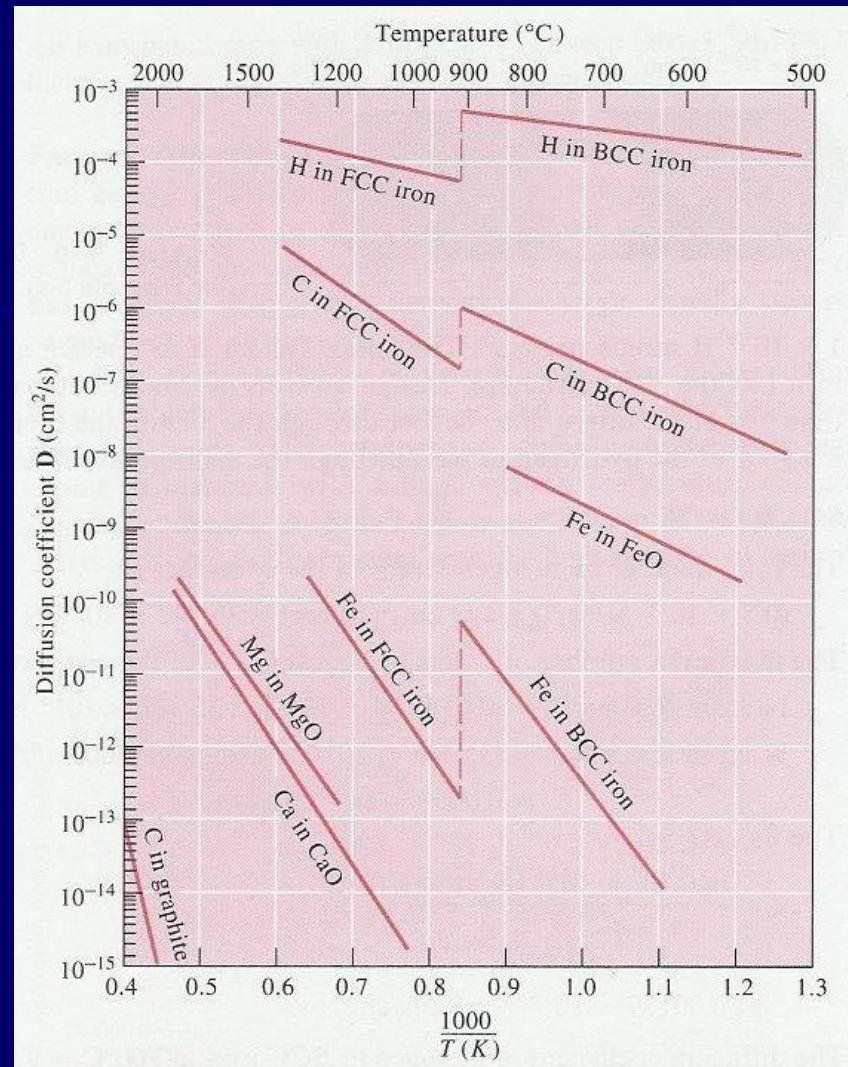
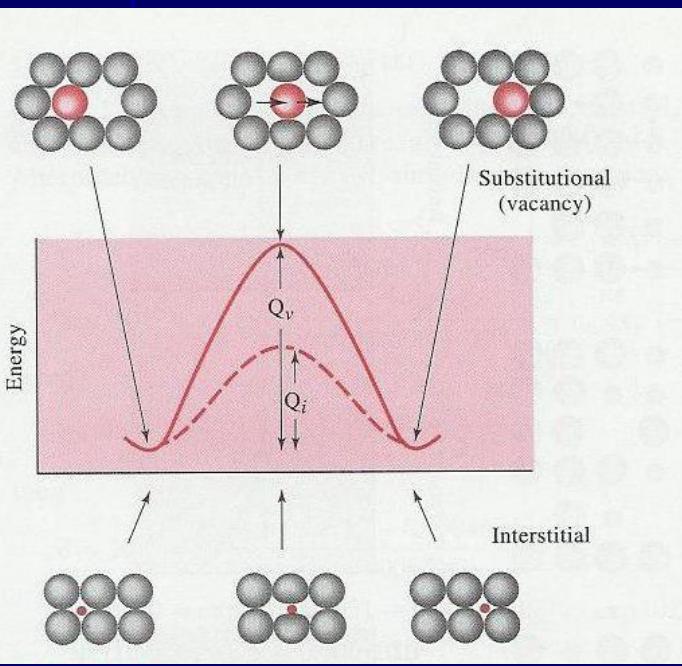
- **Interstitial diffusion - C in Fe, H in Ti, etc.**
- **Vacancy diffusion**
- **Self diffusion, tracer diffusion - healing of defects, time-dependent mechanical phenomena**
- **Chemical diffusion - diffusion of one element through another, solid state chemical reactions**
  
- **Bulk diffusion**
- **Diffusion in grain boundaries, lattice defects**
- **Surface diffusion**
  
- **Diffusion is a statistical phenomenon, driven by the random motion of atoms.**



**Diffusion is a thermally activated process, resulting in an exponential temperature dependence:**

$$D = D_0 \exp(-Q/kT)$$

**It can also depend on orientation relative to the crystal axes.**



**Interstitials diffuse much faster than substitutional impurities and matrix atoms.**

# Phenomenological description

**Fick's law:**

$$\mathbf{j}_D = -\nabla c$$

$j_D$  in  $\text{cm}^2/\text{s}$ ;  $c$  in particles/ $\text{cm}^3$

**Continuity:**

$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{j}_D = 0$$

**Combined:**

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c)$$

If  $D = \text{const.}$

$$\frac{\partial c}{\partial t} = D \nabla^2 c$$

To be solved for  $c(x,t)$  or  $c(r,t)$

Typical solution depends on  $x/(Dt)^{1/2}$ .

One can define a diffusion front that travels as  $x^2 \sim 6Dt$

If defined that way, about 99% of the diffusing element is still behind the diffusion front.



# Rough correlations

- $D_0$  for self diffusion in metals  $\sim 1 \text{ cm}^2/\text{s}$  (0.1 to 10)
- $\Delta H_D / T_m \sim 1.5 \times 10^{-3} \text{ eV/K}$
- $\Delta H_D / L_m \sim 15$

These relationships are useful if no measured data are available. Typically estimates of diffusion are quite rough, there is a huge variation, high accuracy is not needed. Also, defects and impurities influence diffusion very much, it is difficult to control it.



# Examples

Temperature is uniformly  $T = 912^\circ\text{C}$ , the alpha-gamma transition of iron.

Diffusion time  $t = 1 \text{ h} = 3600 \text{ s}$ , distance  $x^2 = 6Dt$

**Self diffusion in alpha Fe:**  $D_0 = 2.0 \text{ cm}^2/\text{s}$ ,  $\Delta H_D = 2.5 \text{ eV}$

$$D = 2.0 \exp(-2.5/8.6 \cdot 10^{-5} \cdot 11850) = 4.4 \cdot 10^{-11} \text{ cm}^2/\text{s}, \quad x \sim 10 \mu\text{m}$$

**Self diffusion in gamma Fe:**  $D_0 = 0.4 \text{ cm}^2/\text{s}$ ,  $\Delta H_D = 2.8 \text{ eV}$

$$D = 4.6 \cdot 10^{-13} \text{ cm}^2/\text{s}, \quad x \sim 1 \mu\text{m}$$

**$^{60}\text{Co}$  in alpha Fe:**  $D_0 = 0.2 \text{ cm}^2/\text{s}$ ,  $\Delta H_D = 2.4 \text{ eV}$

$$D = 1.2 \cdot 10^{-11} \text{ cm}^2/\text{s}, \quad x \sim 5 \mu\text{m}$$

**C in alpha Fe:**  $D_0 = 0.004 \text{ cm}^2/\text{s}$ ,  $\Delta H_D = 0.83 \text{ eV}$

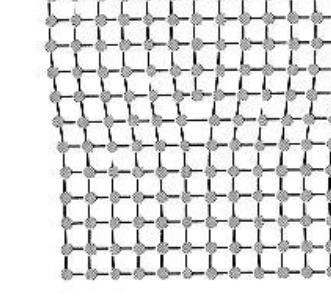
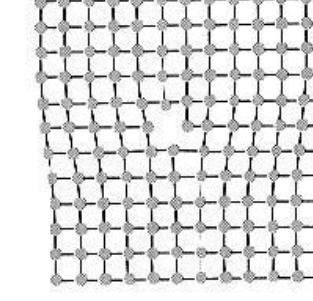
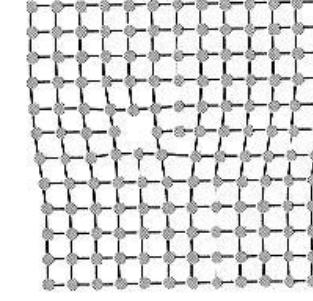
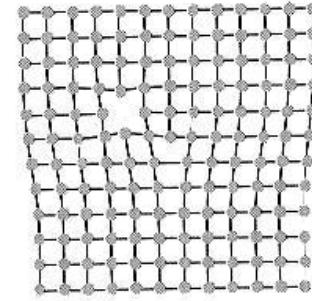
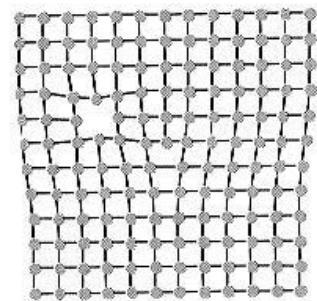
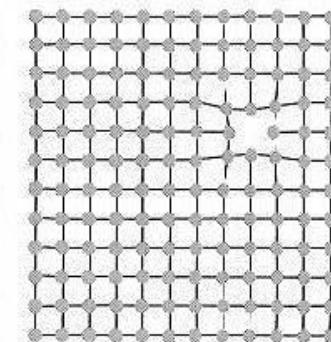
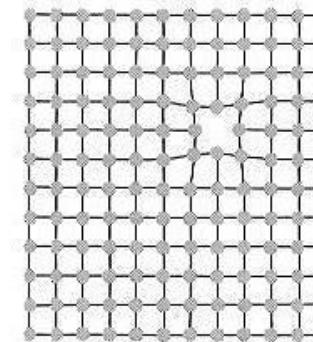
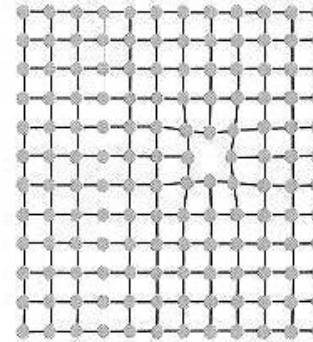
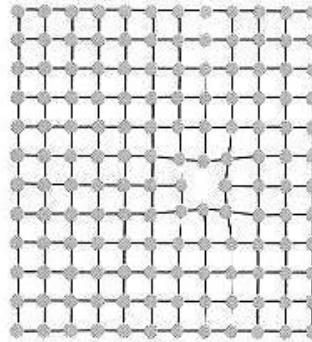
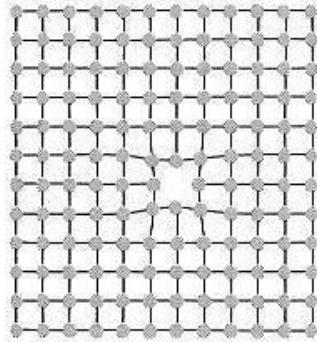
$$D = 1.2 \cdot 10^{-6} \text{ cm}^2/\text{s}, \quad x \sim 1.6 \text{ mm}$$

**C in gamma Fe:**  $D_0 = 0.67 \text{ cm}^2/\text{s}$ ,  $\Delta H_D = 1.6 \text{ eV}$

$$D = 1.0 \cdot 10^{-7} \text{ cm}^2/\text{s}, \quad x \sim 0.5 \text{ mm}$$

Notice the very large differences.

# Vacancy diffusion in a solid and dislocation climb due to capturing vacancies



# Surface and interface diffusion

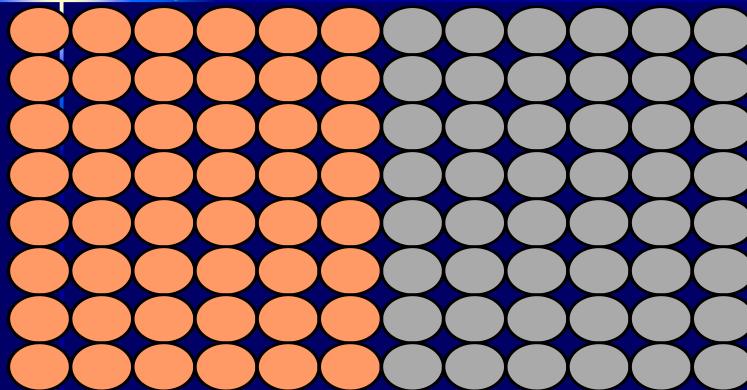
- More open, diffusion can take place faster. In fact, dislocations provide routes for fast diffusion also. Diffusion in grain boundaries makes predicting the behavior of polycrystals difficult.
- Activation energy is lowest for surface diffusion, larger for grain boundary diffusion, and the highest for bulk diffusion. Therefore, bulk diffusion dominates at high temperature (larger number of possible sites) but grain boundary and surface diffusion takes over at lower temperature.
- Technological importance: Thin film deposition, weakening of grain boundaries by impurities, shape changes of particles, etc.
- Diffusion can be accelerated by introducing grain boundaries and other lattice defects. This is an important benefit from MA (mechanical alloying).



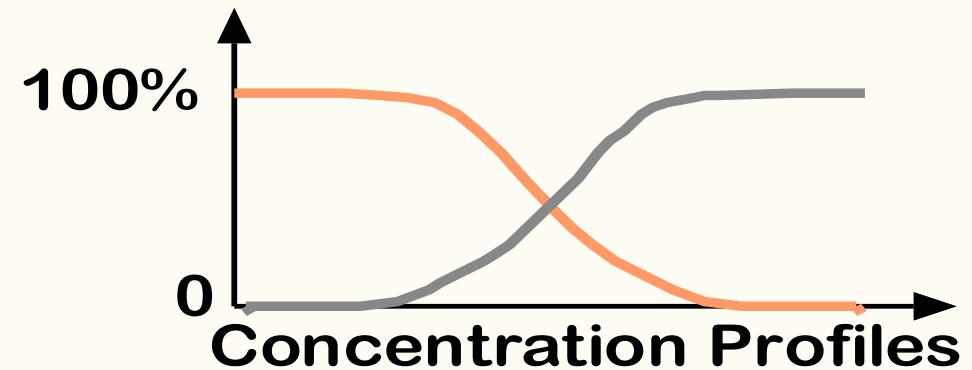
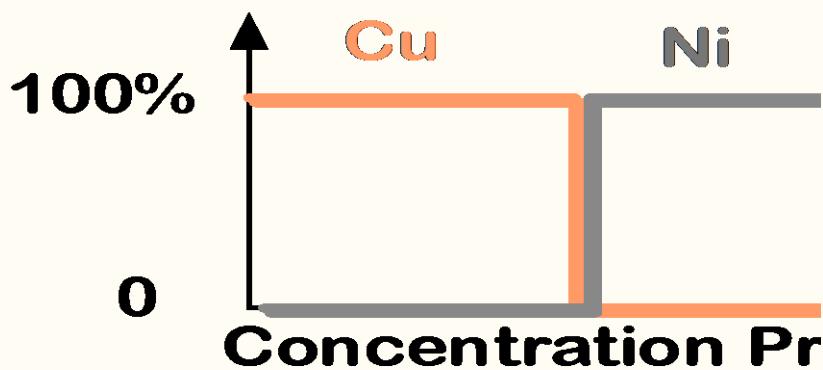
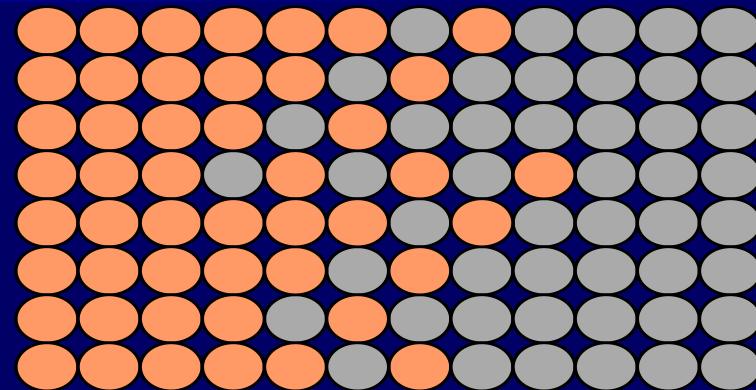
# Interdiffusion

- Interdiffusion: in alloys, atoms tend to migrate from regions of large concentration.

Initially



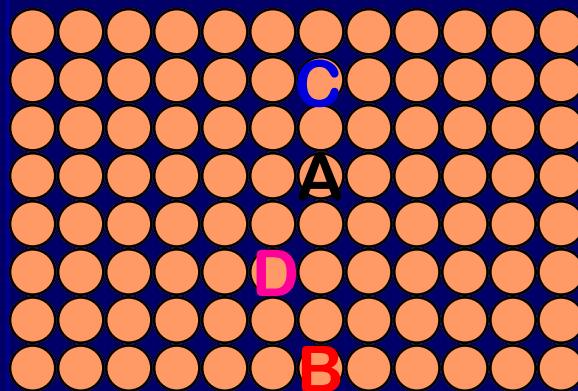
After some time



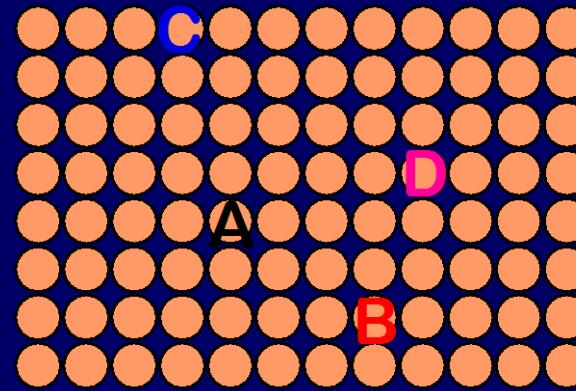
## Self diffusion

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

Label some atoms



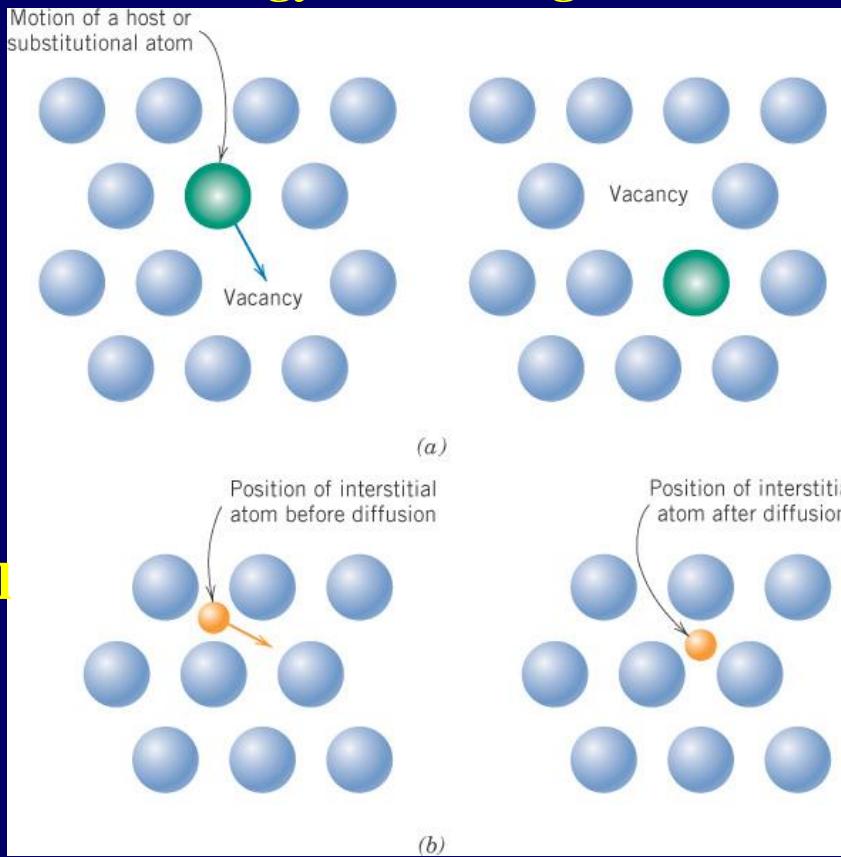
After some time



This can be observed on metal surface under UHV conditions with scanning tunneling microscopy

# Vacancy diffusion or interstitial diffusion

- applies to substitutional impurities
- atoms exchange with vacancies
- *rate* depends on
  - (1) number of vacancies
  - (2) activation energy to exchange.



Concentration of Vacancies  
at temp T

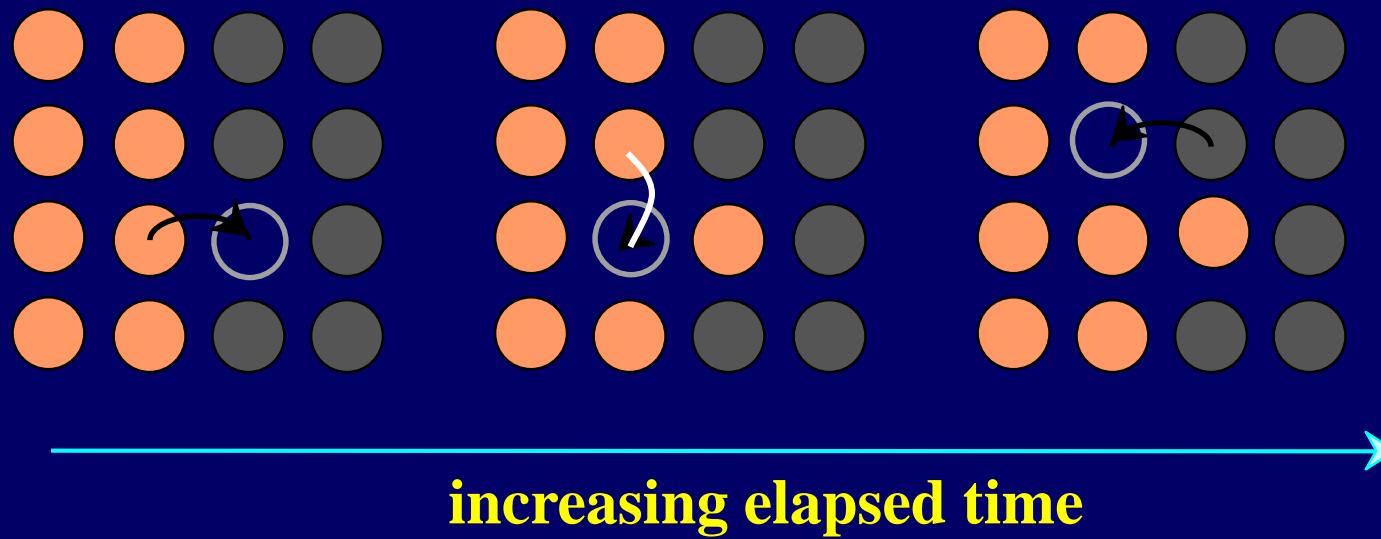
$$c_i = \frac{n_i}{N} e^{-\frac{\Delta E}{K_B T}}$$

The two processes have  
an activation energy  
(eV/atom).

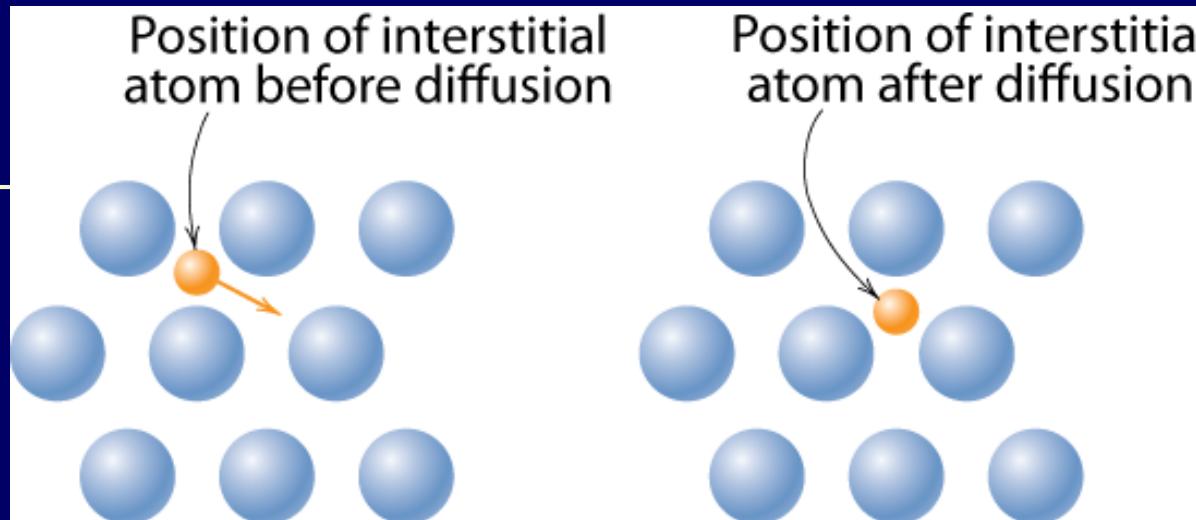
# Substitution-diffusion

## Vacancy Diffusion:

- applies to substitutional impurities
- atoms exchange with vacancies
- *rate depends on* (1) number of vacancies;  
(2) activation energy to exchange.



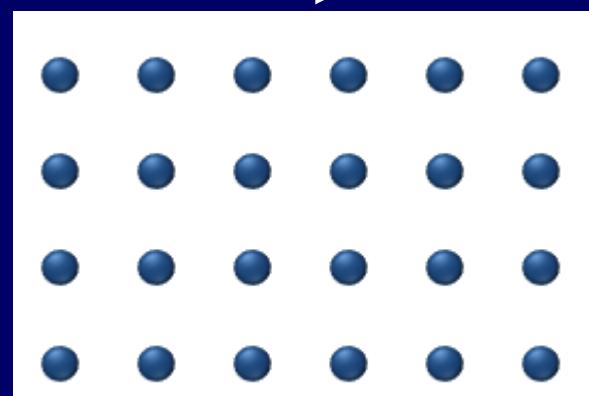
## Interstitial diffusion



- Interstitial diffusion – smaller atoms diffuse between atoms.

**More rapid than vacancy diffusion**

**Concentration gradient**



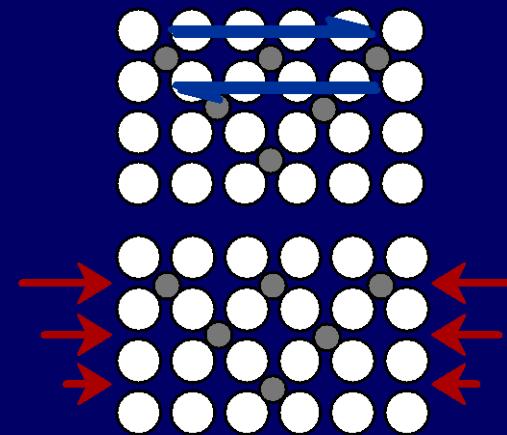
# Processing using Diffusion

- **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.



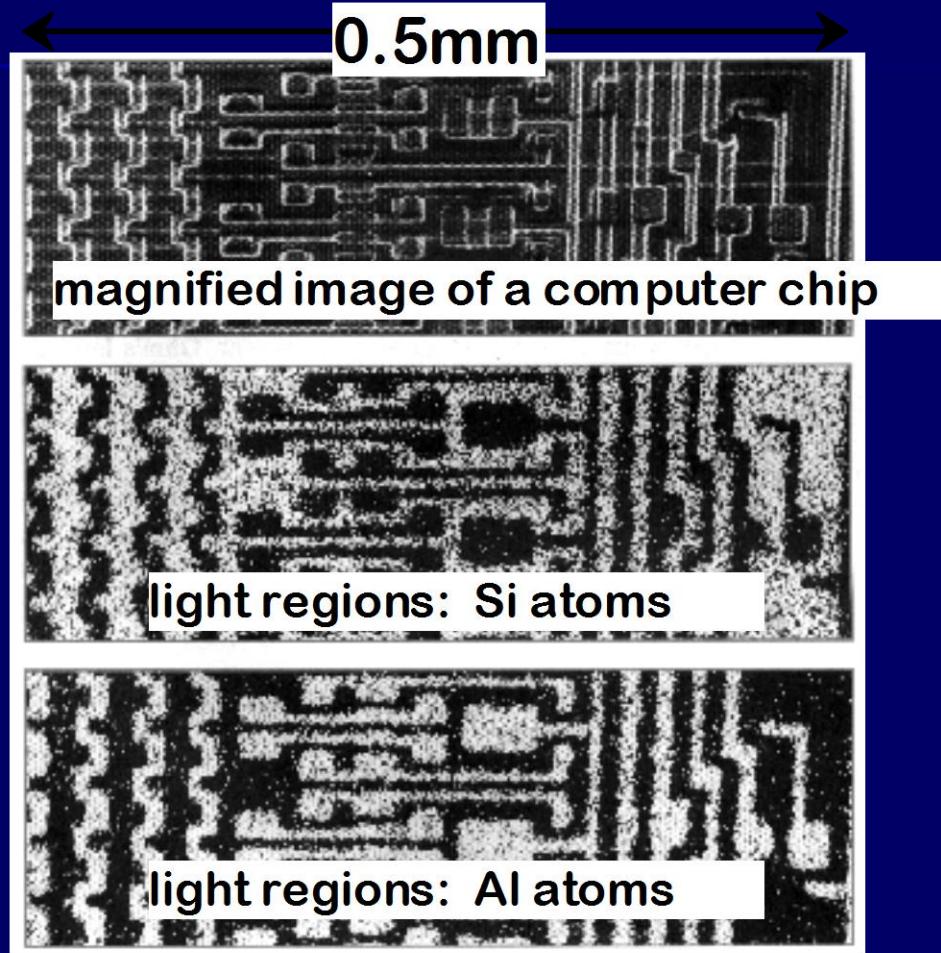
# Processing using Diffusion

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

1. Deposit P rich layers on surface.



2. Heat it.  
3. Result: Doped semiconductor regions.

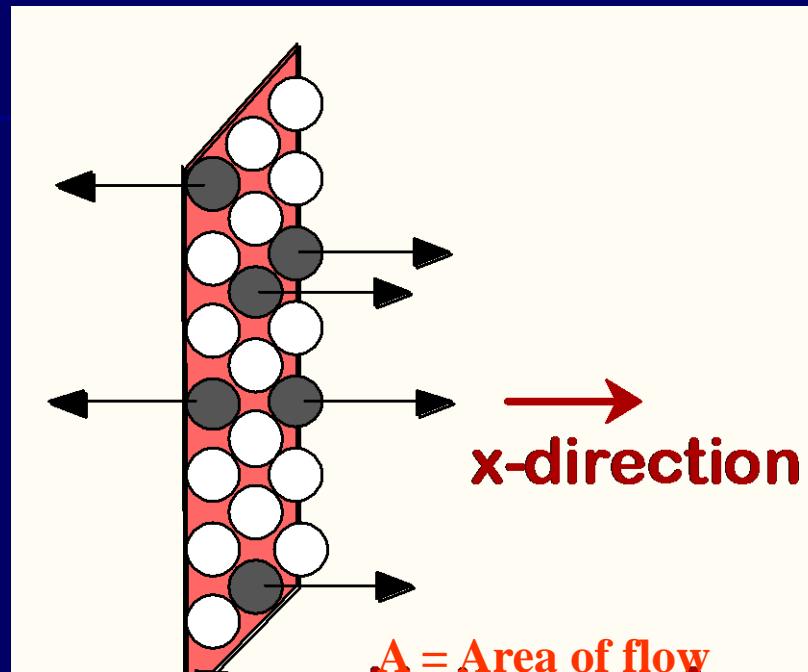


# Modeling rate of diffusion: flux

- Flux:

$$Q_m = \frac{1}{A} \frac{dM}{dt}$$

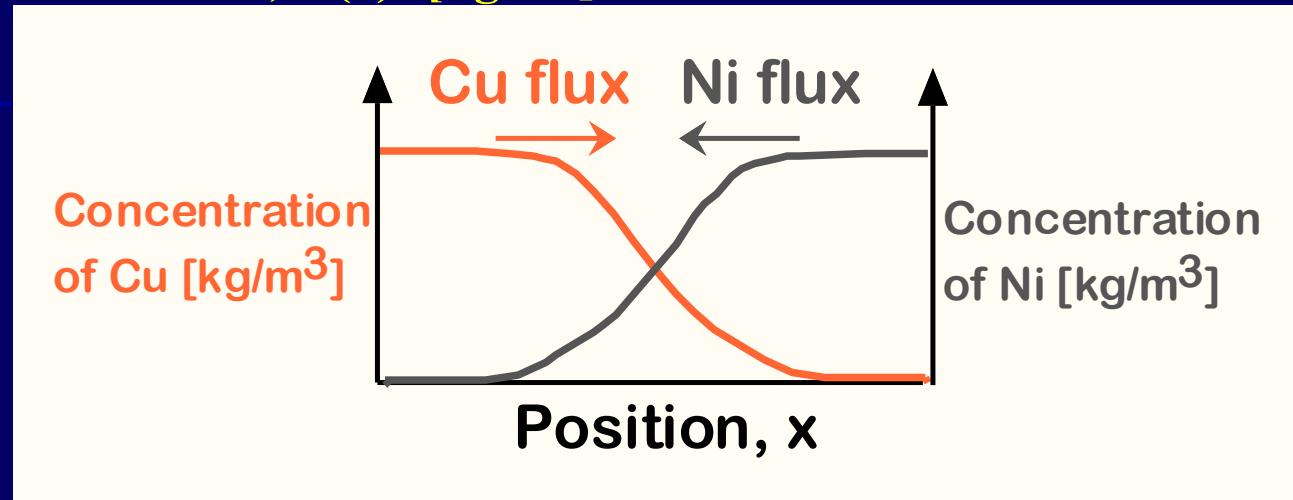
- Flux can be measured for:
  - vacancies
  - host (A) atoms
  - impurity (B) atoms
- Empirically determined:
  - Make thin membrane of known surface area
  - Impose concentration gradient
  - Measure how fast atoms or molecules diffuse through the membrane



**A = Area of flow**

# Steady-state Diffusion

- Concentration Profile,  $C(x)$ : [kg/m<sup>3</sup>]



- Fick's First Law:

$$Q_{m,x} = -D \frac{dC}{dx}$$

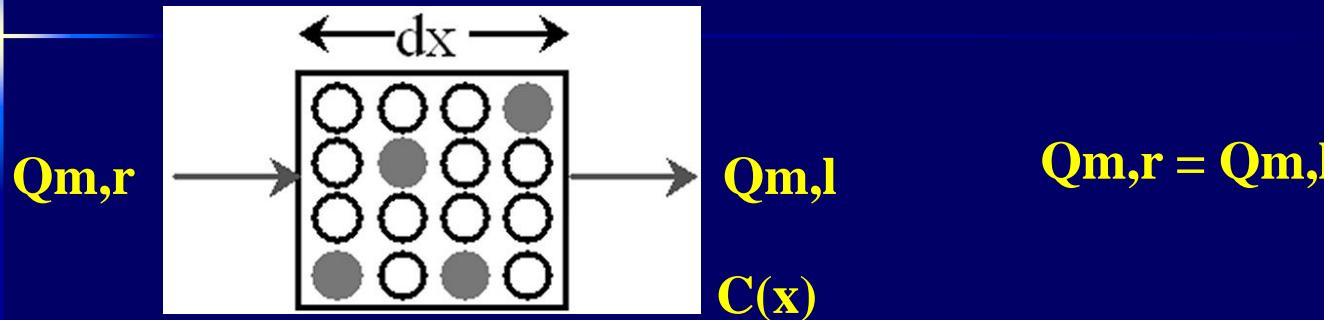
$$D = \text{m}^2/\text{s}$$

D=diffusion coefficient

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

# Steady-State Diffusion

- Steady State: concentration profile not changing with time.



- Apply Fick's First Law:

$$Q_{m,x} = -D \frac{dC}{dx}$$

- since  $Q_{m,l} = Q_{m,r}$  then

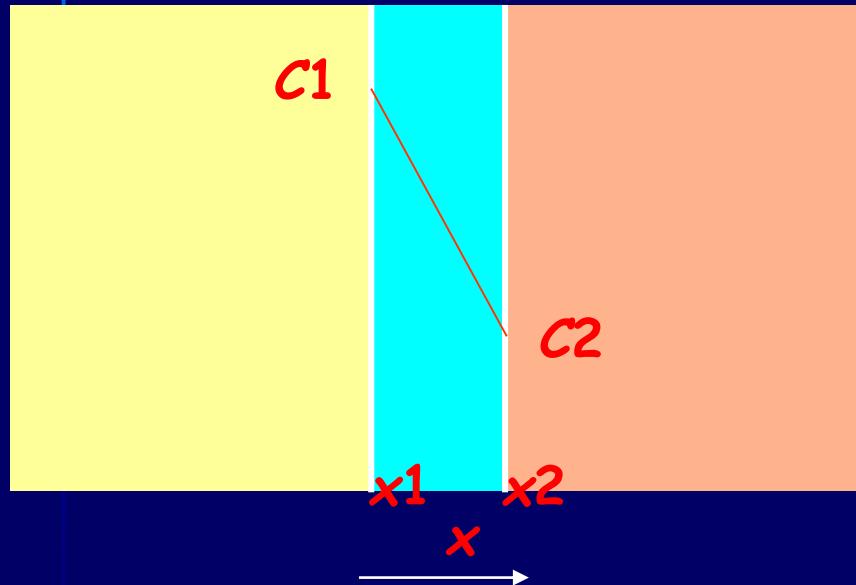
$$\frac{dC}{dx}_{left} = \frac{dC}{dx}_{right}$$

The slope,  $dC/dx$ , must be constant (i.e., doesn't vary with position)

# Steady-State Diffusion

Rate of diffusion independent of time

$$Q_{m,x} = -D \frac{dC}{dx}$$



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

# Example: C Diffusion in steel plate

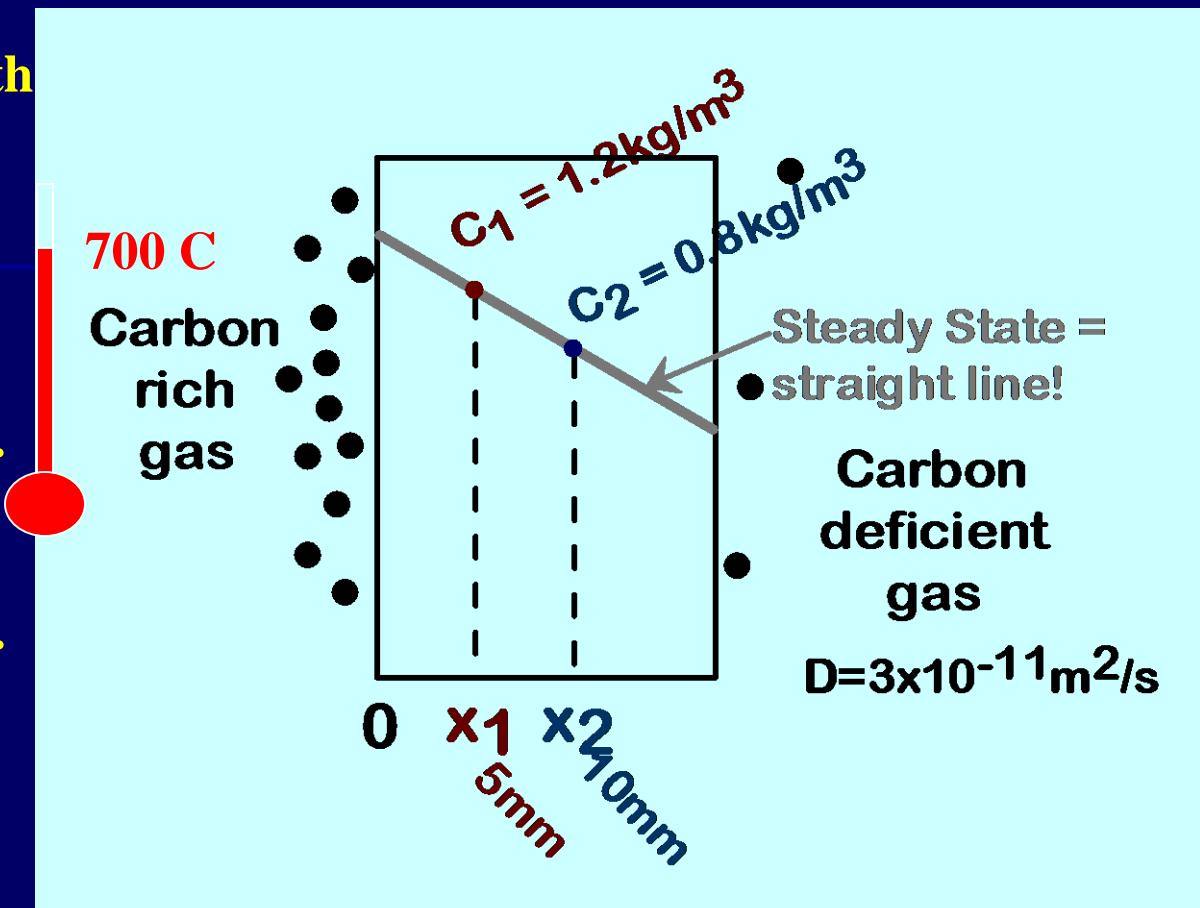
- Steel plate at 700°C with geometry shown:

Knowns:

$C_1 = 1.2 \text{ kg/m}^3$  at 5mm  
( $5 \times 10^{-3} \text{ m}$ ) below surface.

$C_2 = 0.8 \text{ kg/m}^3$  at 10mm  
( $1 \times 10^{-2} \text{ m}$ ) below surface.

$D = 3 \times 10^{-11} \text{ m}^2/\text{s}$  at 700 C.



In steady-state, how much carbon transfers from the rich to the deficient side?

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

## Example: Chemical Protection Clothing

Methylene chloride is a common ingredient of paint removers. Besides being an irritant, it also may be absorbed through skin. When using, 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:

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

surface concentrations:  $C_1 = 0.44 \text{ g/cm}^3$      $C_2 = 0.02 \text{ g/cm}^3$

Diffusion distance:     $x_2 - x_1 = 0.04 \text{ cm}$

$$J_x = -D \frac{C_2 - C_1}{x_2 - x_1} = 1.16 \times 10^{-5} \frac{\text{g}}{\text{cm}^2\text{s}}$$

# Example: Diffusion of radioactive atoms

- Surface of Ni plate at  $1000^{\circ}\text{C}$  contains 50%  $\text{Ni}^{60}$  (radioactive) and 50% Ni (non-radioactive).
- 4 microns below surface  $\text{Ni}^{60}/\text{Ni} = 48:52$
- Lattice constant of Ni at  $1000\text{ C}$  is  $0.360\text{ nm}$ .
- Experiment shows that self-diffusion of Ni is  $1.6 \times 10^{-9} \text{ cm}^2/\text{sec}$

What is the flux of  $\text{Ni}^{63}$  atoms through a plane  $2\text{ }\mu\text{m}$  below surface?

$$C_1 = \frac{(4\text{Ni/cell})(0.5\text{Ni}^{63}/\text{Ni})}{(0.36 \times 10^{-9}\text{ m})^3/\text{cell}} \\ = 42.87 \times 10^{27} \text{ Ni}^{63}/\text{m}^3$$

$$C_2 = \frac{(4\text{Ni/cell})(0.48\text{Ni}^{63}/\text{Ni})}{(0.36 \times 10^{-9}\text{ m})^3/\text{cell}} \\ = 41.15 \times 10^{27} \text{ Ni}^{63}/\text{m}^3$$

$$\mathbf{J} = -D \frac{C_2 - C_1}{x_2 - x_1} = -(1.6 \times 10^{-13} \text{ m}^2/\text{sec}) \frac{(41.15 - 42.87) \times 10^{27} \text{ Ni}^{63}/\text{m}^3}{(4 - 0) \times 10^{-6} \text{ m}} \\ = +0.69 \times 10^{20} \text{ Ni}^{63}/\text{m}^2 \cdot \text{s}$$

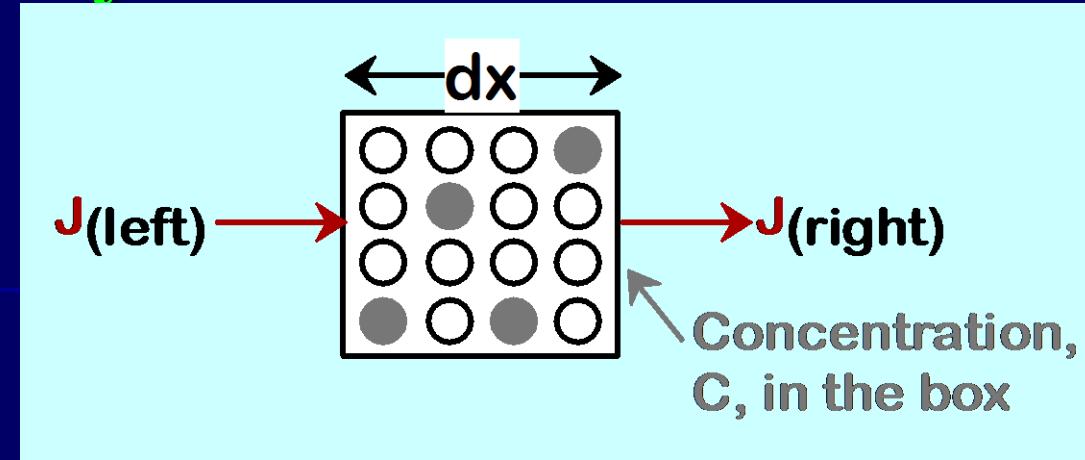
How many  $\text{Ni}^{63}$  atoms/second through cell?

$$J \cdot (0.36\text{nm})^2 = 9 \text{ Ni}^{63}/\text{s}$$



# Non-Steady-State Diffusion

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



- To conserve matter:

- Fick's First Law:

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

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

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

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

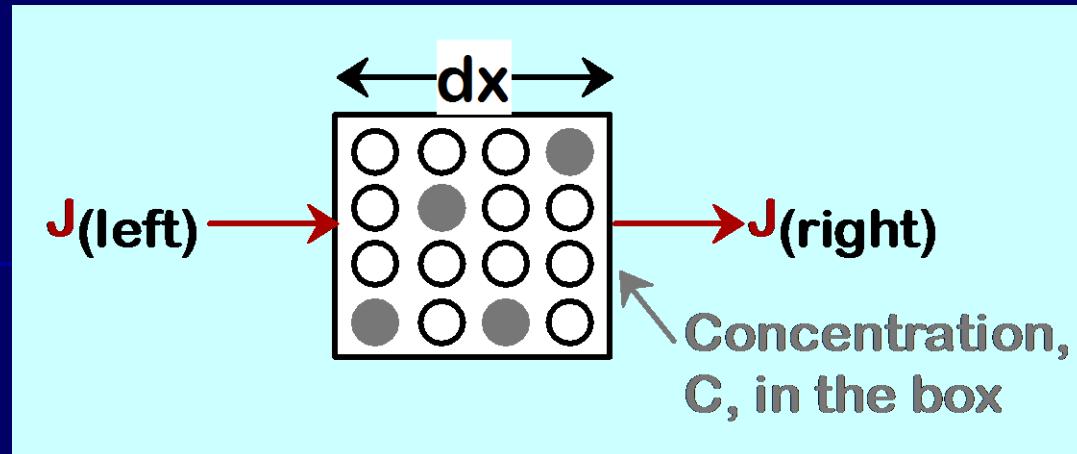
**equate**

- Governing Eqn.:

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

# Non-Steady-State Diffusion: another look

- Concentration profile,  $C(x)$ , changes w/ time.
- Rate of accumulation  $C(x)$



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

$$\rightarrow \frac{\partial C}{\partial t} dx = J_x - (J_x + \frac{\partial J_x}{\partial x} dx) = -\frac{\partial J_x}{\partial x} dx$$

- Using Fick's Law:
- If D is constant:

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

Fick's  
2nd Law

Fick's Second "Law"

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

# Non-Steady-State Diffusion: $C = c(x,t)$

concentration of diffusing species is a function of both time and position

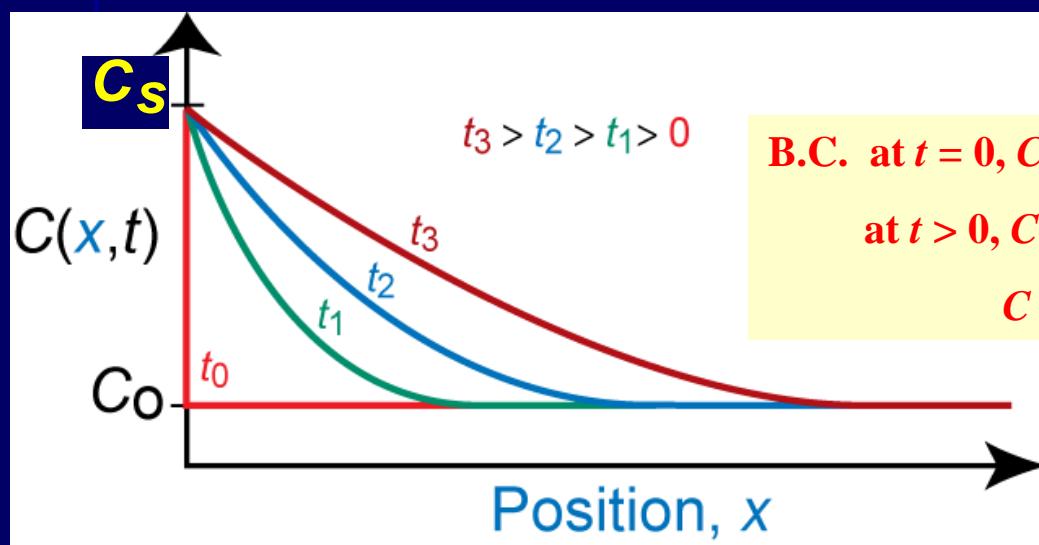
Fick's Second "Law"  $\frac{\partial C}{\partial t} \approx \left( D \frac{\partial C^2}{\partial x^2} \right)$

- Copper diffuses into a bar of aluminum.

Surface conc.,  
 $C_S$  of Cu atoms



pre-existing conc.,  $C_0$  of copper atoms



B.C. at  $t = 0, C = C_0$  for  $0 \leq x \leq \infty$

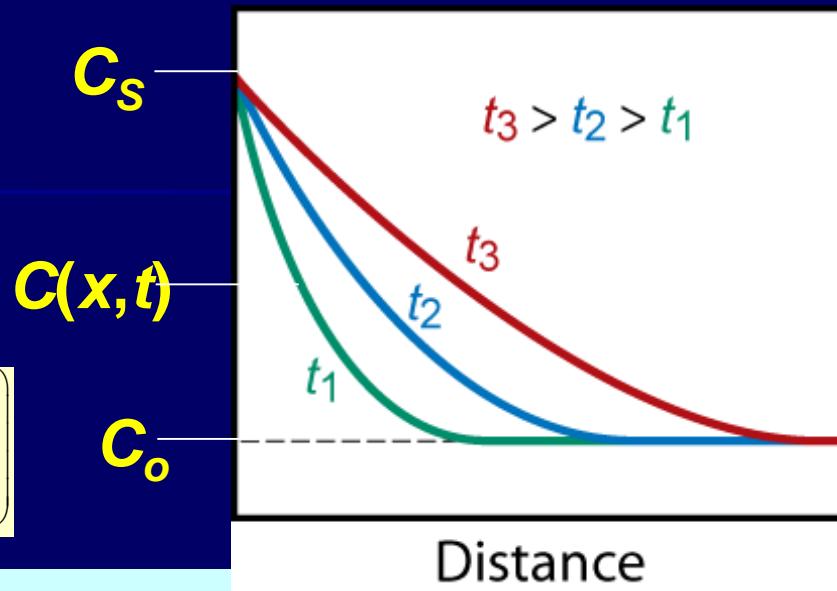
at  $t > 0, C = C_S$  for  $x = 0$  (fixed surface conc.)

$C = C_0$  for  $x = \infty$

Adapted from Fig. 6.5,  
Callister & Rethwisch 3e.

# Non-Steady-State Diffusion

- Cu diffuses into a bar of Al.



- 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 6.1

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

# Example: Non-Steady-State Diffusion

FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere that gives a surface C content 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, what temperature was treatment done?

**Solution**

$$\frac{C(x,t) - C_o}{C_s - C_o} = \frac{0.35 - 0.20}{1.0 - 0.20} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 1 - \operatorname{erf}(z) \quad \therefore \operatorname{erf}(z) = 0.8125$$

Using Table 6.1 find z where  $\operatorname{erf}(z) = 0.8125$ . Use interpolation.

$z$	$\operatorname{erf}(z)$
0.90	0.7970
$z$	0.8125
0.95	0.8209

$$\frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970} \quad \text{So, } z = 0.93$$

Now solve for  $D$

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

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

## Solution (cont.):

- To solve for the temperature at which  $D$  has the above value, we use a rearranged form of Equation (6.9a);

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

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

- From Table 6.2, for diffusion of C in FCC Fe

$$D_o = 2.3 \times 10^{-5} \text{ m}^2/\text{s} \quad Q_d = 148,000 \text{ J/mol}$$

$$D = 2.6 \times 10^{-11} \text{ m}^2/\text{s}$$

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

$$T = 1300 \text{ K} = 1027^\circ\text{C}$$

# Example: Processing

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

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.

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

- Answer:

$$t_{500} = \frac{(Dt)_{600}}{D_{500}} = \frac{10 \text{ hrs}}{\frac{5.3 \times 10^{-13} \text{ m}^2/\text{s}}{4.8 \times 10^{-14} \text{ m}^2/\text{s}}} = 110 \text{ hr}$$

Note  
 $D(T)$  are T dependent!  
Values of D are provided.

# Diffusion and Temperature

- Diffusivity increases with T exponentially (so does Vacancy conc.).

$$D = D_0 \exp \left( - \frac{E_{ACT}}{R T} \right)$$

$D$  = diffusion coefficient [m<sup>2</sup>/s]

$D_0$  = pre-exponential [m<sup>2</sup>/s]

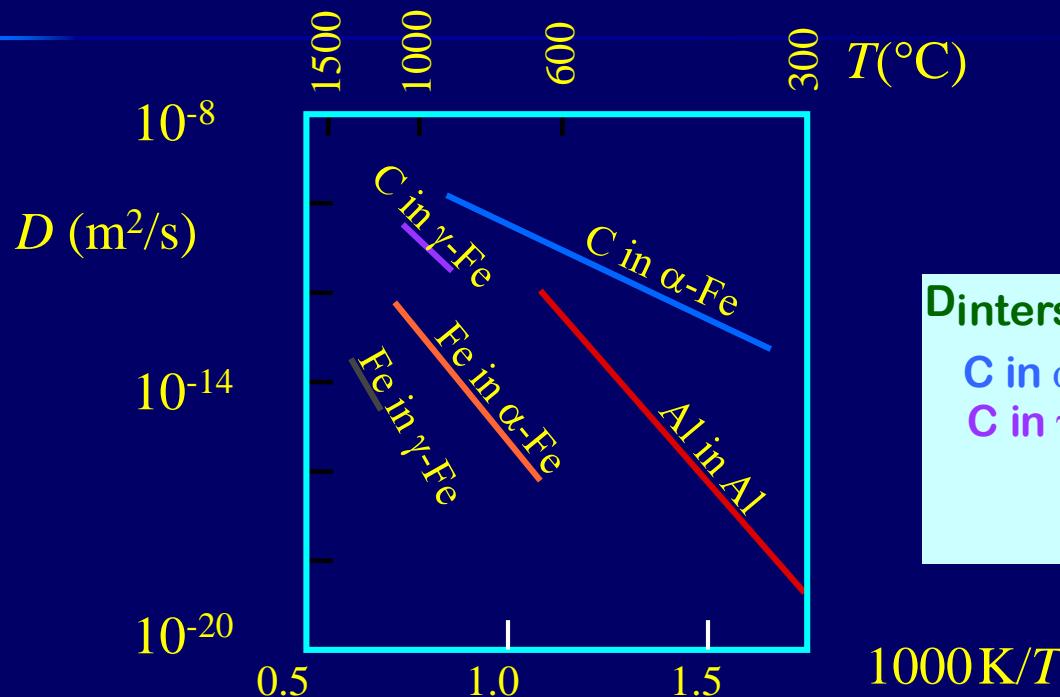
$E_{ACT}$  = activation energy [J/mol or eV/atom]

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

$T$  = absolute temperature [K]



- Experimental Data:



$D_{\text{interstitial}} >> D_{\text{substitutional}}$

C in  $\alpha$ -Fe  
C in  $\gamma$ -Fe

Cu in Cu  
Al in Al  
Fe in  $\alpha$ -Fe  
Fe in  $\gamma$ -Fe  
Zn in Cu

Callister & Rethwisch 3e.

from E.A. Brandes and G.B. Brook (Ed.) Smithells Metals Reference Book, 7th ed., Butterworth-Heinemann, Oxford, 1992.)

# Example: Comparing Diffuse in Fe

Is C in fcc Fe diffusing faster than C in bcc Fe?

fcc-Fe:  $D_0=2.3 \times 10^{-5} \text{ (m}^2/\text{s)}$

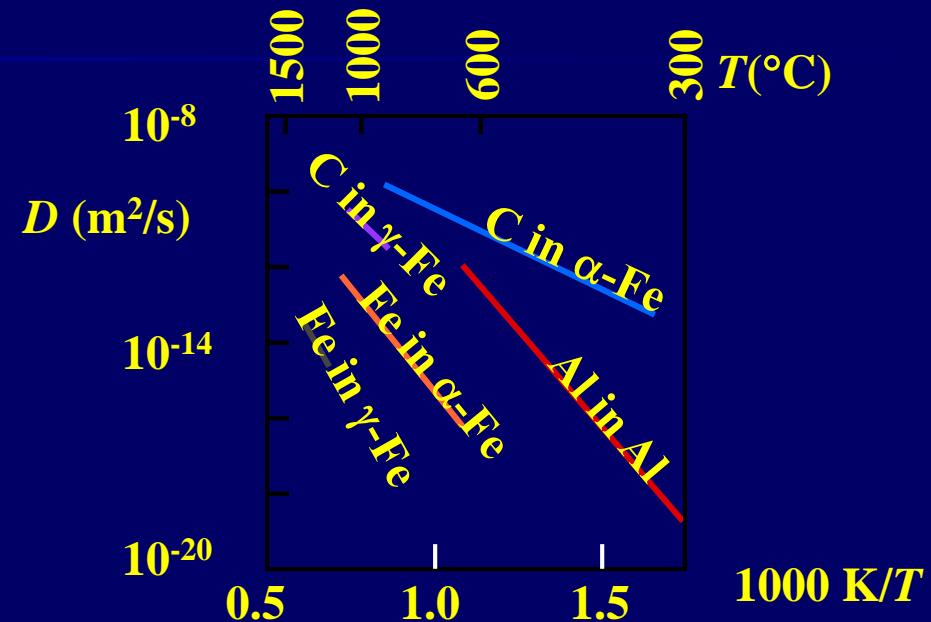
EACT=1.53 eV/atom

T = 900 C D=  $5.9 \times 10^{-12} \text{ (m}^2/\text{s)}$

bcc-Fe:  $D_0=6.2 \times 10^{-7} \text{ (m}^2/\text{s)}$

EACT=0.83 eV/atom

T = 900 C D=  $1.7 \times 10^{-10} \text{ (m}^2/\text{s)}$



- FCC Fe has both higher activation energy EACT and  $D_0$  (holes larger in FCC). BCC and FCC phase exist over limited range of T (at varying %C). Hence, at same T, BCC diffuses faster due to lower EACT.
- Cannot always have the phase that you want at the %C and T you want! which is why this is all important.

# More than one diffusing species

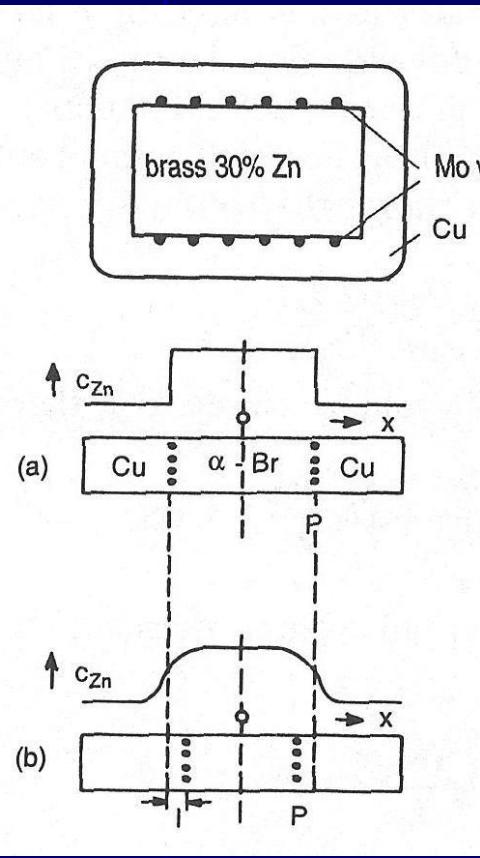
**Diffusion is usually asymmetric, the boundary between regions is shifting, often difficult to define.**

**Very importantly, solid state reactions always take place at interfaces via diffusion. The products form intermediate layers that often act as diffusion barriers. Decreasing the particle size - e.g. by ball milling - accelerates the reactions.**

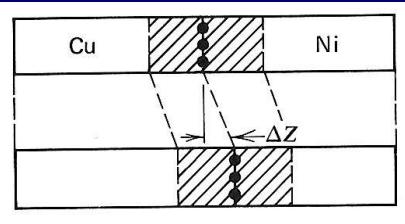
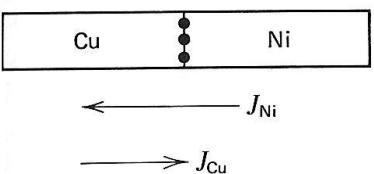
**Diffusion relates to volume changes, formation of voids, etc.**

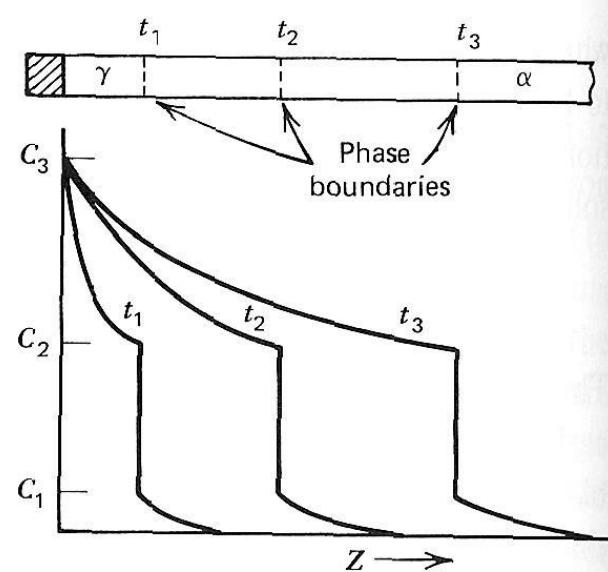
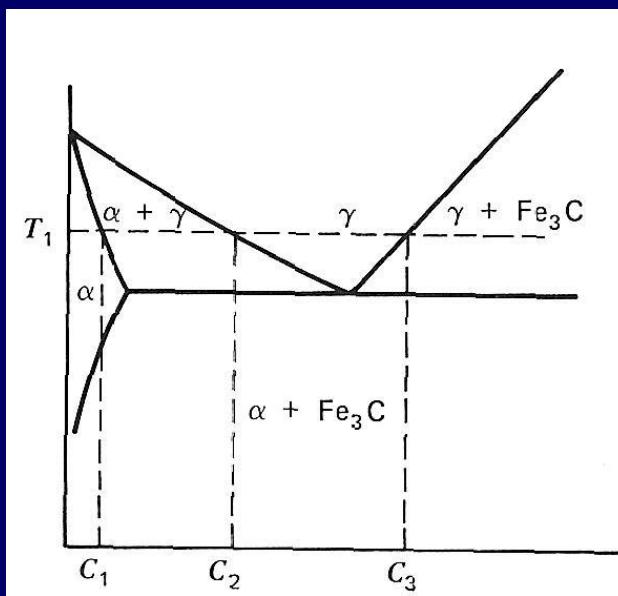
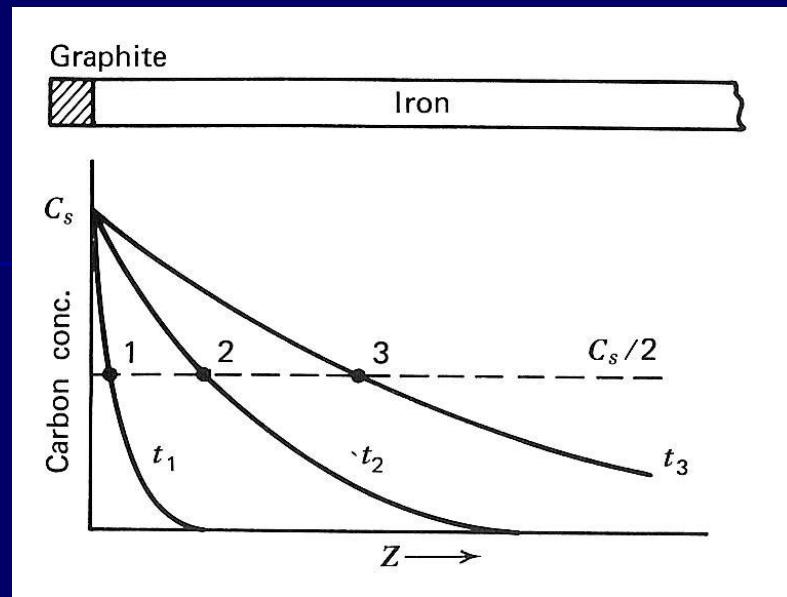
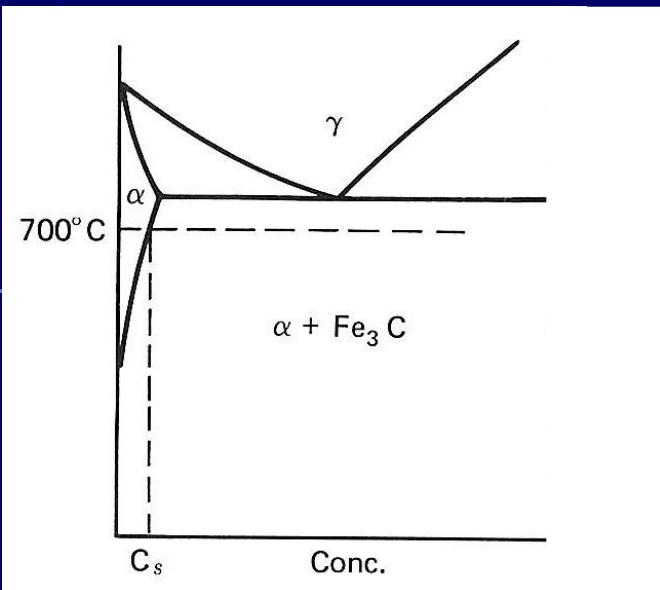


# The Kirkendall experiment

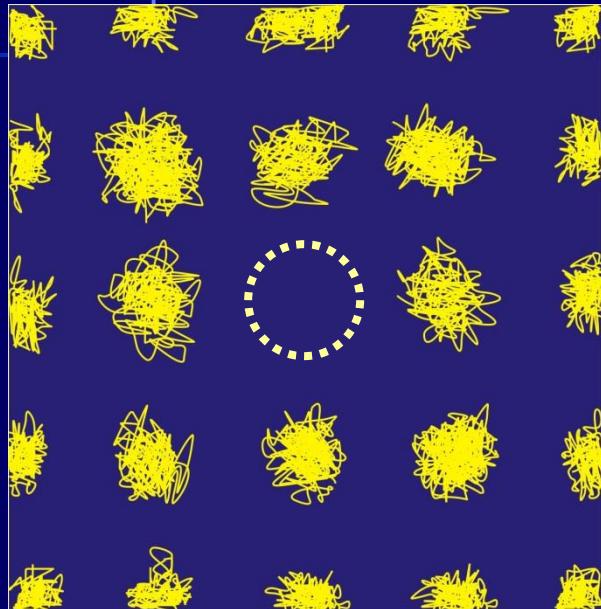


**Zn diffuses faster than Cu in this system. As a result, the Cu - brass interface shifts, the Mo wires marking the interface drift toward each other.**





# *Diffusion coefficient: Tracer*



$$D_i^* = (w * l^2) * f$$

**Di\***= tracer diffusion coefficient

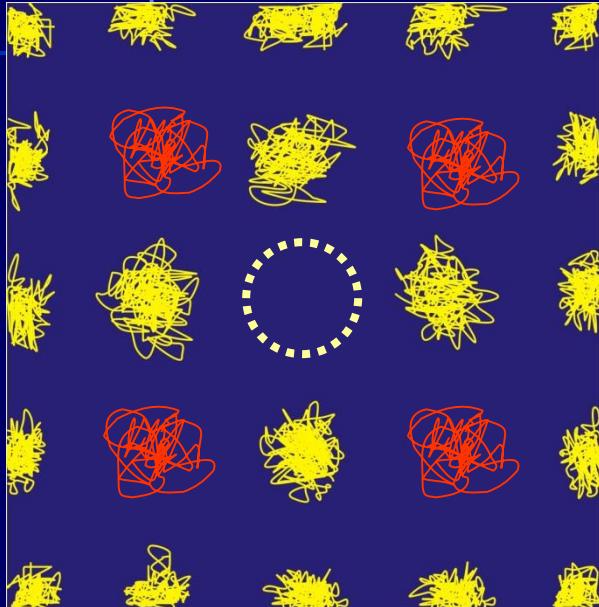
w = frequency of a jump to an adjacent site

l = distance of the jump

f = related to symmetry, coordination number

e.g., diffusion of  $^{56}\text{Fe}$  in homogenous olivine  $(\text{Mg}, \text{Fe})_2\text{SiO}_4$

# *Diffusion coefficient: multicomponent*



$$D_{ij} = D_i^* \delta_{ij} - \left( \frac{D_i^* C_i}{\sum_{k=1}^n D_k^* C_k} \right) (D_j^* - D_n^*)$$

Multicomponent formulation (Lasaga, 1979) for ideal system, elements with the same charge and exchanging in the same site

e.g., diffusion of FeMg olivine

$$D_{FeMg} = \frac{D_{Fe}^* D_{Mg}^*}{X_{Fe} D_{Fe}^* + X_{Mg} D_{Mg}^*}$$

# Diffusion coefficient

Perform experiments at controlled conditions to determine  $D^*$  or  $D_{\text{FeMg}}$

$$D = D_o \exp \left( \frac{-Q - \Delta V (P - 10^5)}{R T} \right)$$

$Q$  = activation energy (at  $10^5$  Pa),  $\Delta V$  = activation volume,  $P$  = pressure in Pascals,  $R$  is the gas constant, and  $D_o$  = pre-exponential factor.

# *Diffusion coefficient*

New experimental and analytical techniques allow to determine D at the conditions (P, T,  $f\text{O}_2$ , ai) relevant for the magmatic processes without need to extrapolation

e.g., Fe-Mg in olivine along [001]

$$D_{\text{Fe-Mg}} = 10^{-9.2} \left( \frac{f\text{O}_2}{10^{-7}} \right)^{1/6} 10^{3(x\text{Fe}-0.1)} \exp \left( - \frac{201\,000 + 7 * 10^{-6} (P - 10^5)}{R T} \right)$$

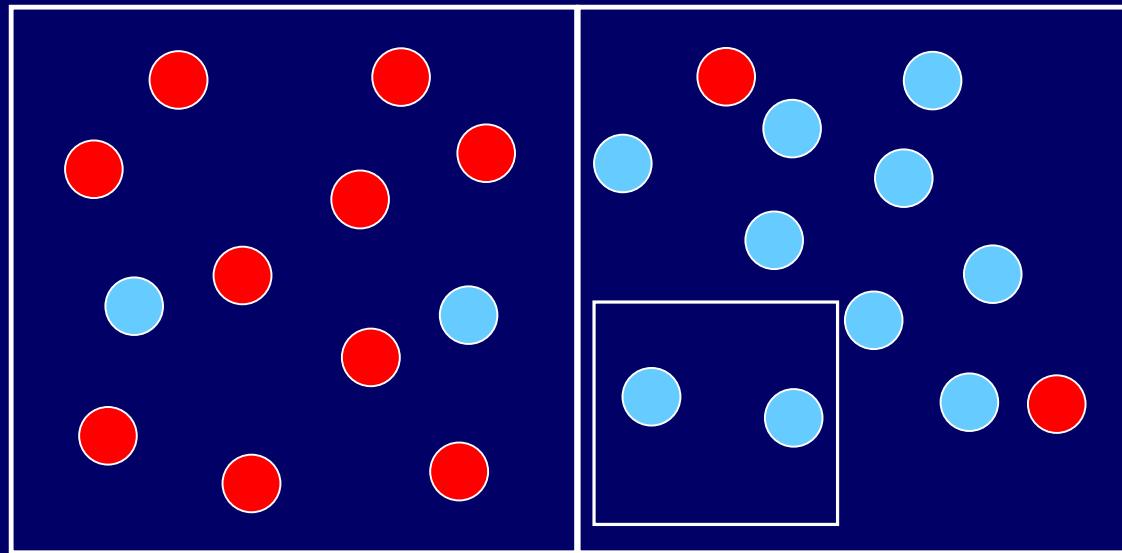
*Dohmen and Chakraborty (2007)*

P.Ravindran, PHY085 – Properties of Materials, 2014 February: [Diffusion and Fick's law](#)



# Continuum Concept

Properties are averaged over small regions of space.



The number of blue circles moving left is larger than the number of blue circles moving right.

We think of concentration as being a point value, but it is averaged over space.

# Diffusion Coefficient

- Probability of a jump is

$$P_j = P_v \cdot P_m = e^{-E_f/kT} \cdot e^{-E_m/kT}$$

Diffusion coefficient is proportional to jump probability

$$D = D_0 e^{-E_D/kT}$$



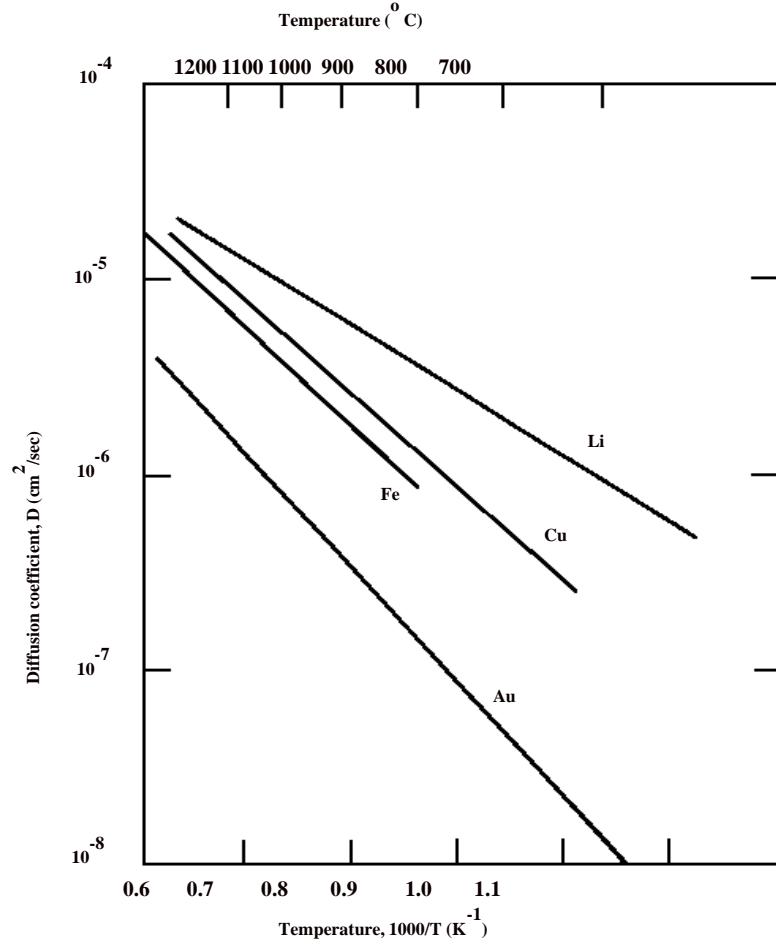
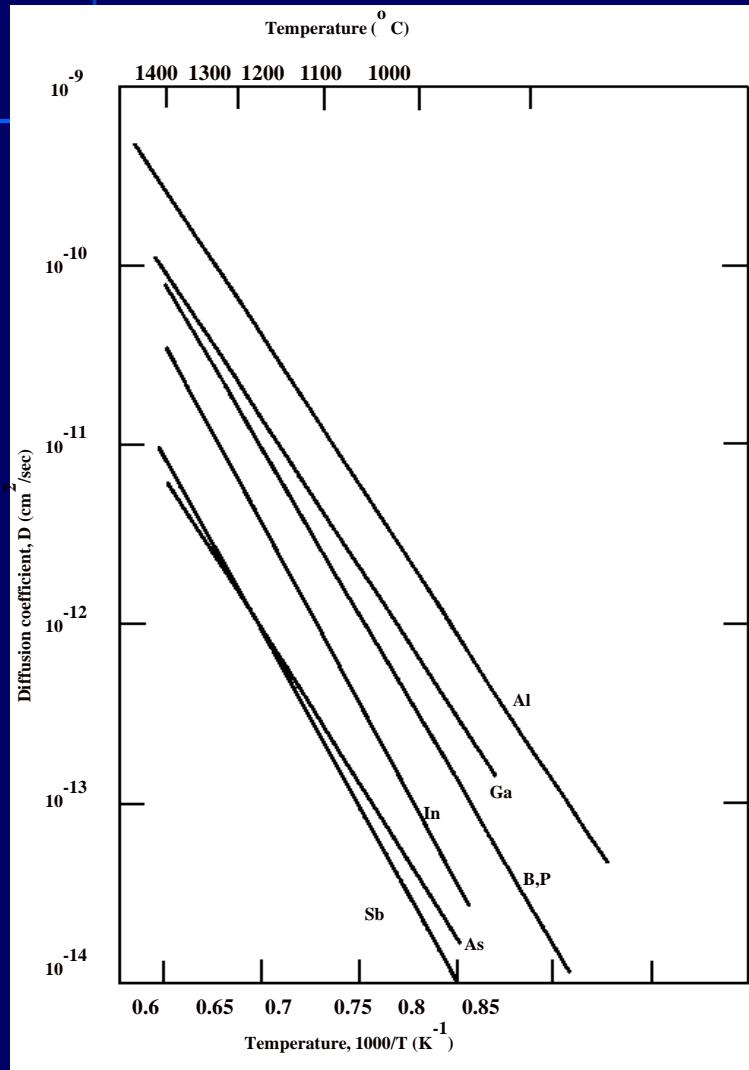
# Diffusion Coefficient

- Typical diffusion coefficients in silicon

Element	$D_o$ (cm <sup>2</sup> /s)	$E_D$ (eV)
B	10.5	3.69
Al	8.00	3.47
Ga	3.60	3.51
In	16.5	3.90
P	10.5	3.69
As	0.32	3.56
Sb	5.60	3.95

# Diffusion Of Impurities In Silicon

- Arrhenius plots of diffusion in silicon



# Diffusion Of Impurities In Silicon

- The intrinsic carrier concentration in Si is about  $7 \times 10^{18}/\text{cm}^3$  at 1000 °C
  - If  $N_A$  and  $N_D$  are  $< n_i$ , the material will behave as if it were intrinsic; there are many practical situations where this is a good assumption



# Diffusion Of Impurities In Silicon

- Dopants cluster into “fast” diffusers (P, B, In) and “slow” diffusers (As, Sb)
  - As we develop shallow junction devices, slow diffusers are becoming very important
  - B is the only p-type dopant that has a high solubility; therefore, it is very hard to make shallow p-type junctions with this fast diffuser



# Successive Diffusions

- To create devices, successive diffusions of n- and p-type dopants
  - Impurities will move as succeeding dopant or oxidation steps are performed
- The effective Dt product is
 
$$(Dt)_{eff} = D_1(t_1 + t_2 + \dots) = D_1t_1 + D_1t_2 + \dots$$
  - No difference between diffusion in one step or in several steps at the same temperature
- If diffusions are done at different temperatures

$$(Dt)_{eff} = D_1t_1 + D_2t_2 + \dots$$



# Successive Diffusions

- The effective  $Dt$  product is given by

$$Dt_{eff} = \sum_i D_i t_i$$

$D_i$  and  $t_i$  are the diffusion coefficient and time for  $i^{\text{th}}$  step

- Assuming that the diffusion constant is only a function of temperature.
- The same type of diffusion is conducted (constant or limited source)

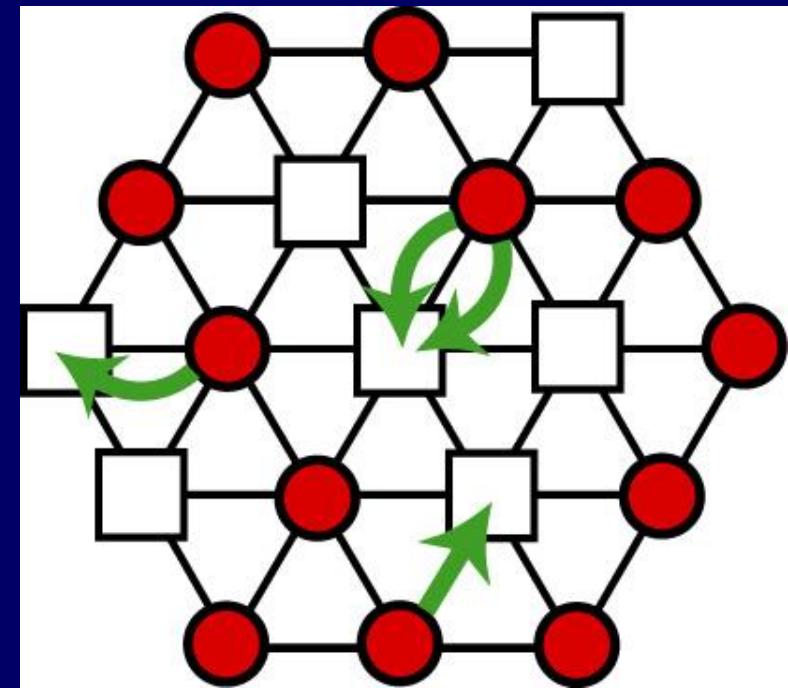
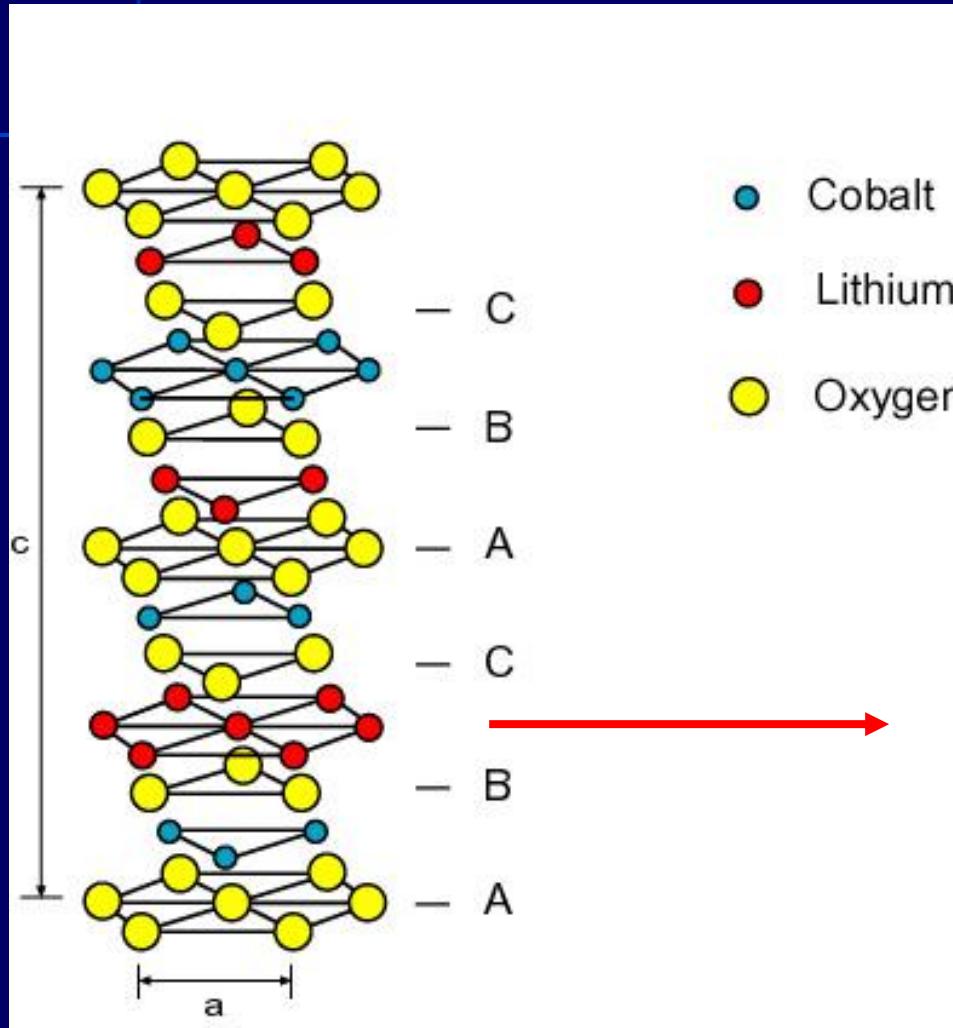
# Interstitial diffusion

- C diffusion in bcc Iron (steel)
- Li diffusion in transition metal oxide host
- O diffusion on Pt-(111) surface

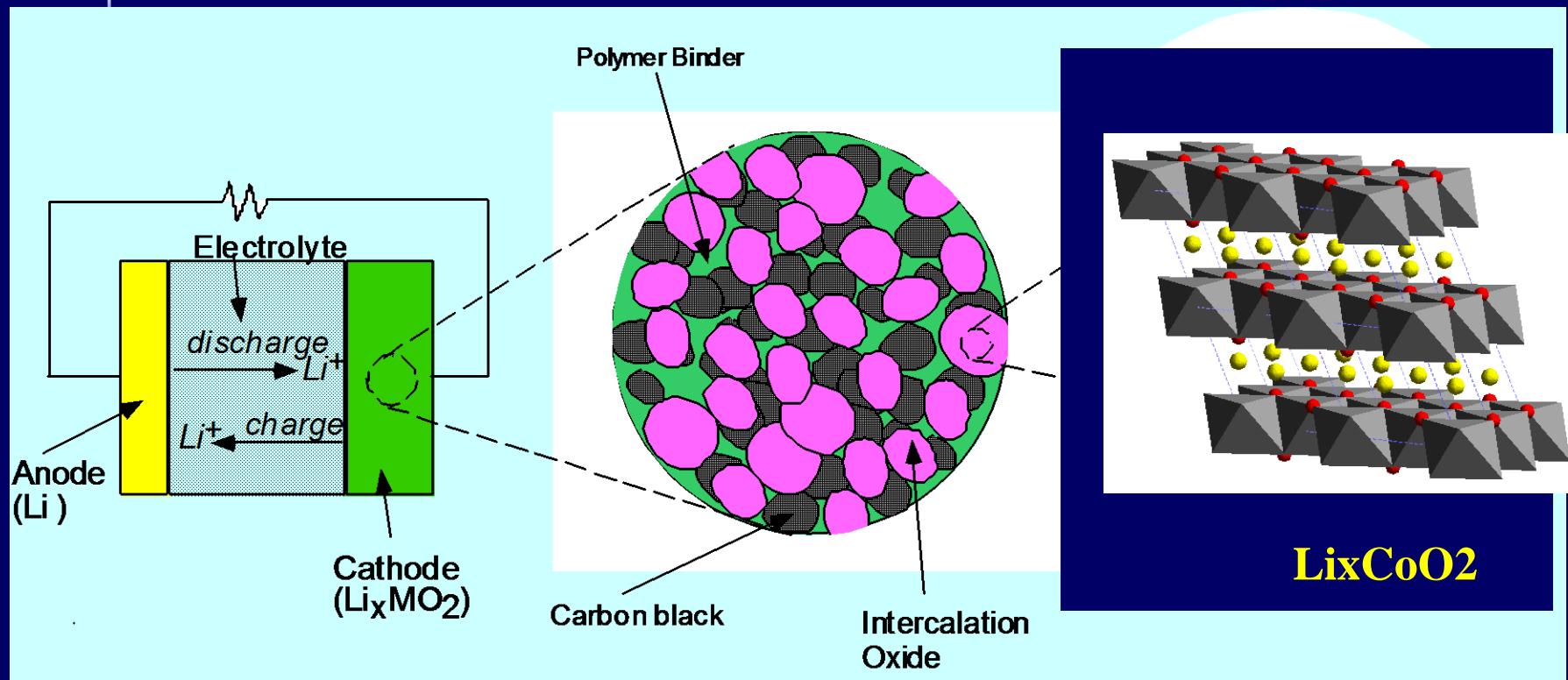
In all examples, diffusion occurs on a rigid lattice which is externally imposed by a host or substrate



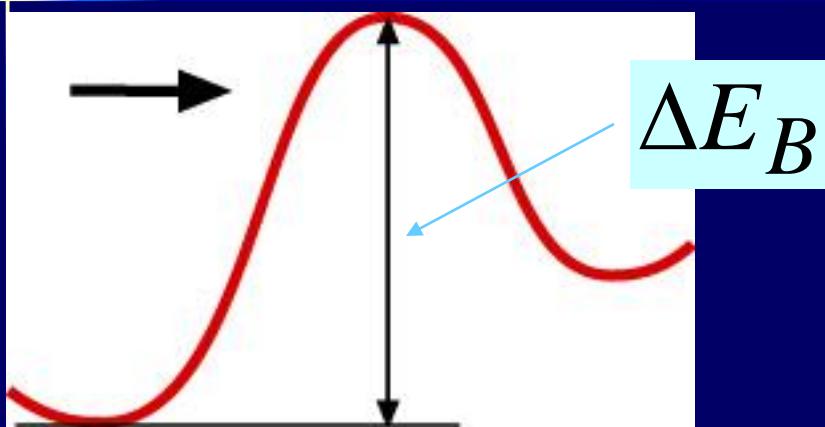
# Example of interstitial diffusion



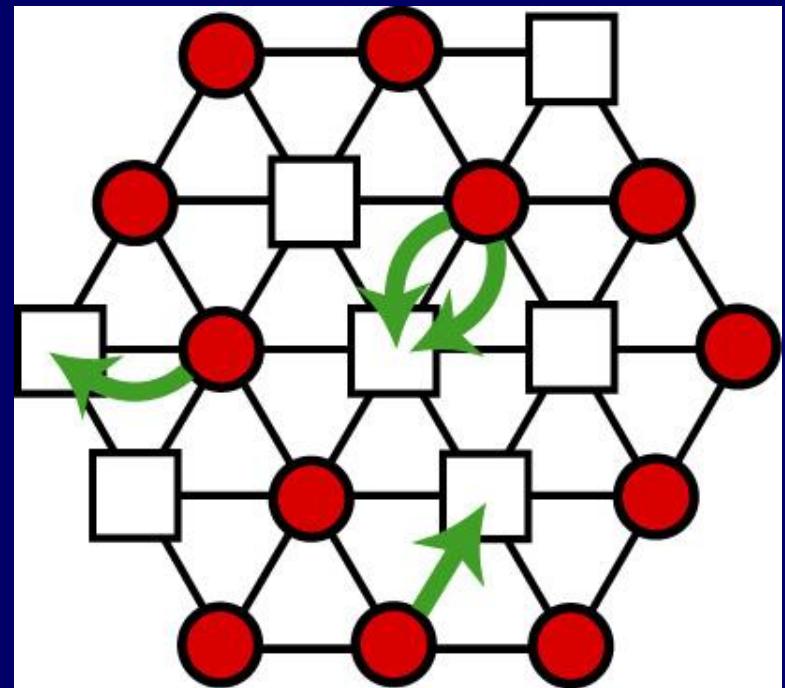
# Intercalation Oxide as Cathode in Rechargeable Lithium Battery



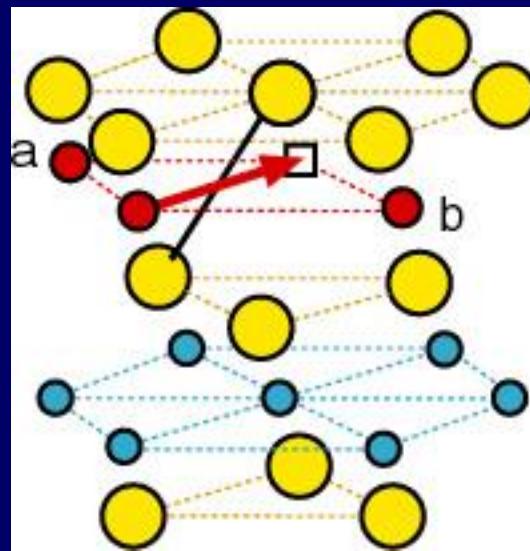
# Individual hops: Transition state theory



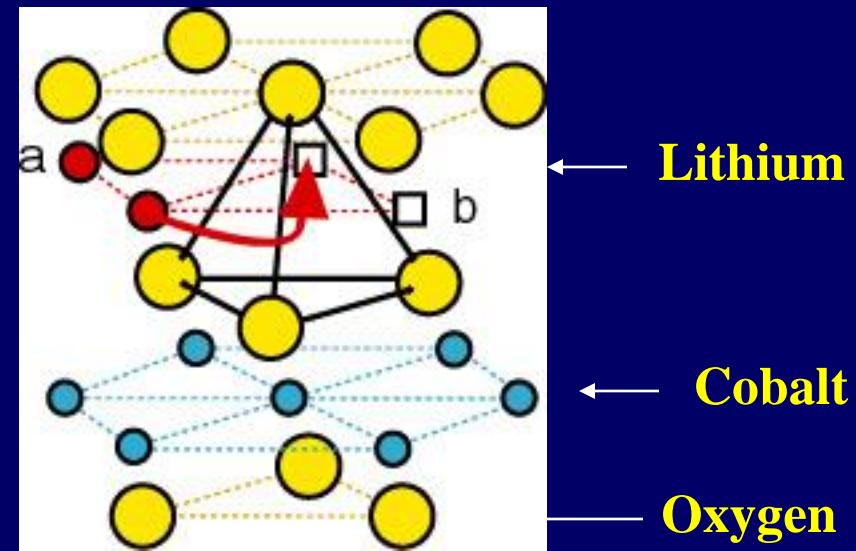
$$\Gamma = v * \exp\left(\frac{-\Delta E_B}{kT}\right)$$



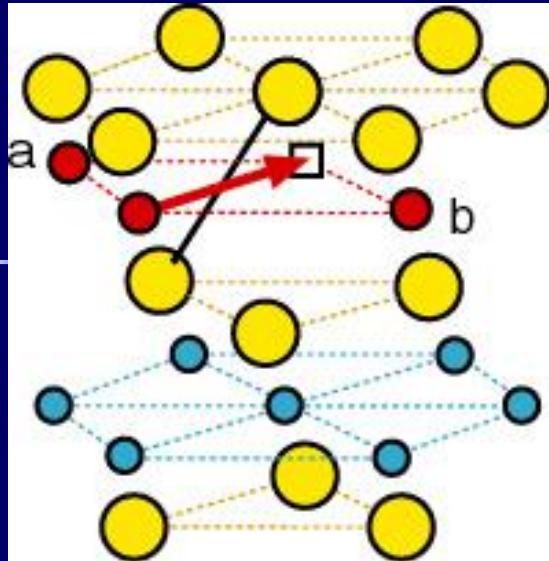
# Migration mechanism in $\text{Li}_x\text{CoO}_2$



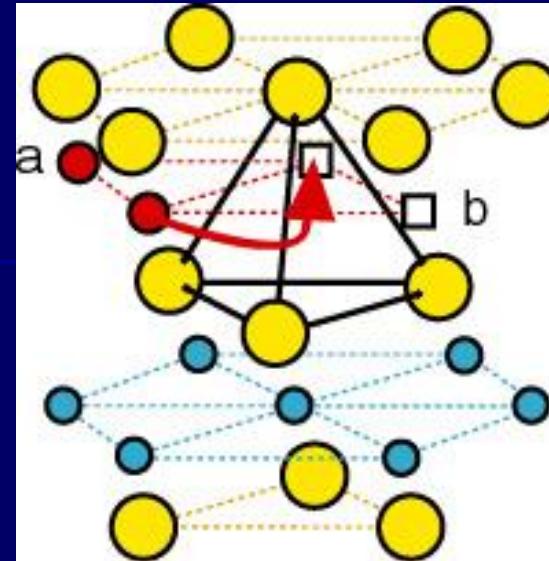
**Single vacancy hop  
mechanism**



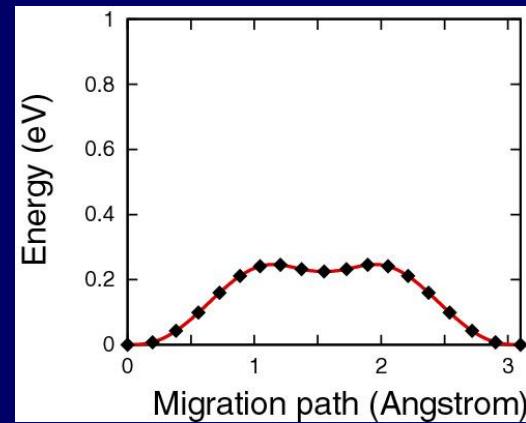
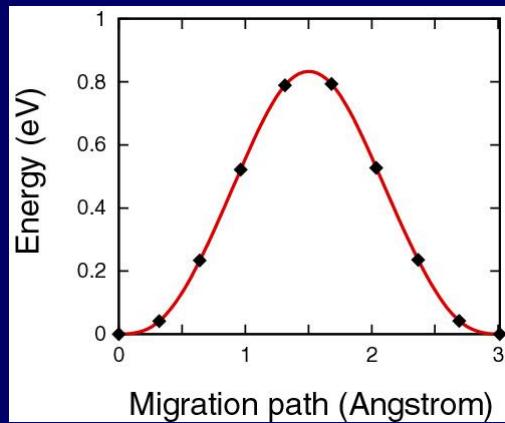
**Divacancy hop  
Mechanism**



Single vacancy hop



Divacancy hop



# Irreversible thermodynamics: interstitial diffusion of one component

$$J = -L \nabla \mu$$

$$D = L \frac{d\mu}{dC}$$

$$J = -D \nabla C$$



# Notation

**M = number of lattice sites**

**N = number of diffusing atoms**

**v<sub>s</sub> = volume per lattice site**

**x = N/M**

**C=x/v<sub>s</sub>**



# Interstitial diffusion: one component

Kubo-Green relations  
(linear response statistical mechanics)

$$D = L \cdot \Theta$$

Thermodynamic factor

$$\Theta = \frac{\partial \mu}{\partial C}$$

Kinetic coefficient

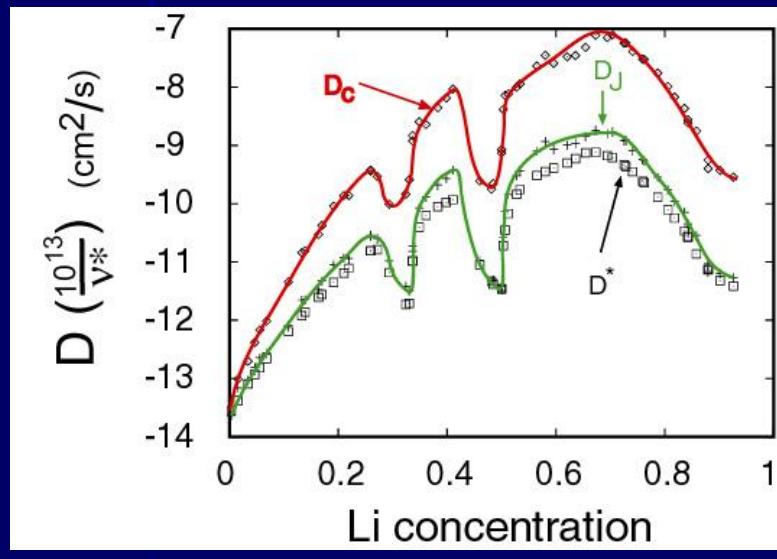
$$L = \frac{1}{(2d)tMv_s k T} \left\langle \left( \sum_{i=1}^N \Delta \vec{R}_i(t) \right)^2 \right\rangle$$

R. Gomer, Rep. Prog. Phys. 53, 917 (1990)/

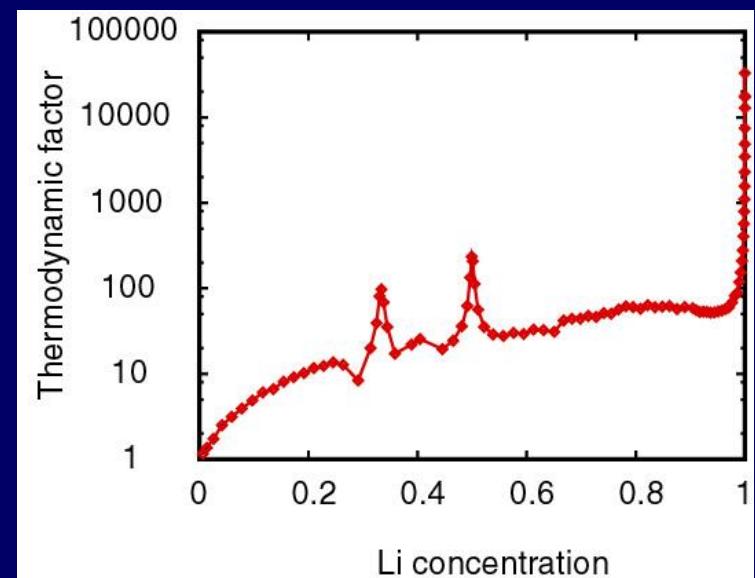
A. Van der Ven, G. Ceder, Handbook of Materials Modeling, chapt. 1.17, Ed. S. Yip, Springer (2005).

$$D = D_J \cdot \tilde{\Theta}$$

**Diffusion coefficient  
at 300 K**



**Thermodynamic  
factor  $\Theta$**



A. Van der Ven, G. Ceder, M. Asta, P.D. Tepesch, Phys Rev. B 64 (2001) 064112

# Interstitial diffusion (two components)

- C & N diffusion in bcc Iron (steel)
- Li & Na diffusion in transition metal oxide host
- O & S diffusion on Pt-(111) surface

In all examples, diffusion occurs on a rigid lattice which is externally imposed by a host or substrate



# Diffusion in an alloy: substitutional diffusion

Not interstitial diffusion

Instead, diffusing atoms form the lattice  
Dilute concentration of vacancies

