

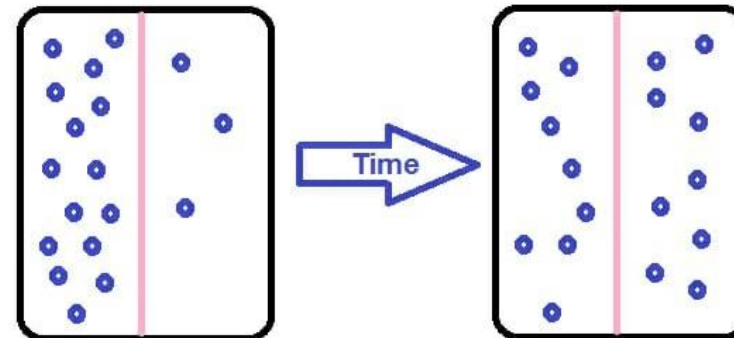
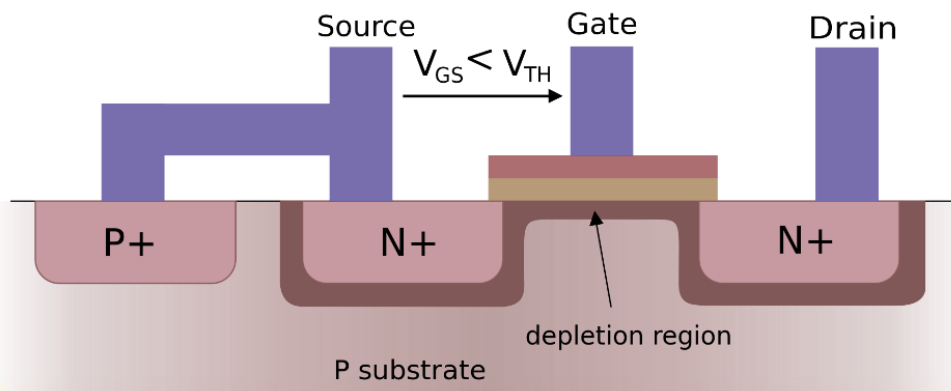
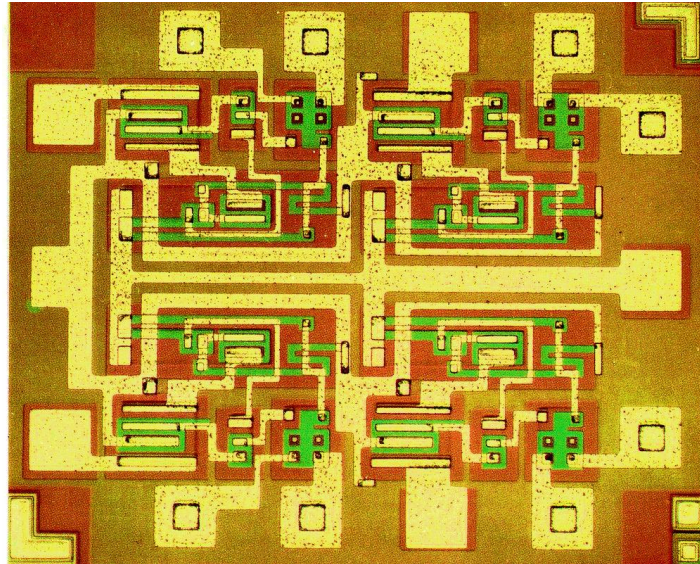


Chapter 5: Diffusion (II)

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Chapter Outline

Diffusion - how do atoms move through solids?

❑ Diffusion mechanisms

Vacancy diffusion

Interstitial diffusion

Impurities

❑ The mathematics of diffusion

Steady-state diffusion (Fick's first law)

Nonsteady-State Diffusion (Fick's second law)

❑ Factors that influence diffusion

Diffusing species

Host solid

Temperature

Microstructure

- **Why is it an important part of processing?**

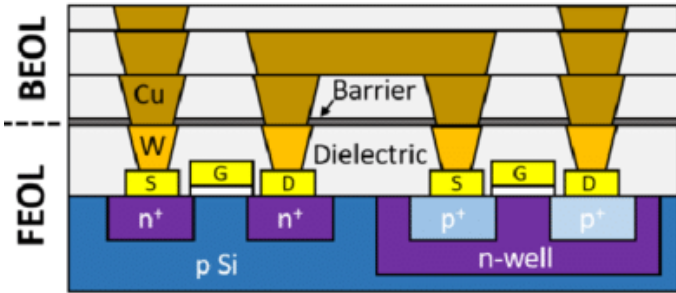
- **How can the rate of diffusion be predicted for some simple cases?**



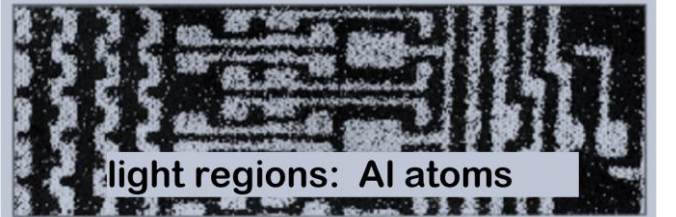
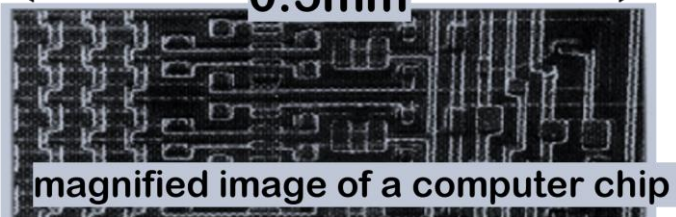


Metal–oxide–semiconductor field-effect transistor (MOSFET)

a, Si CMOS chip

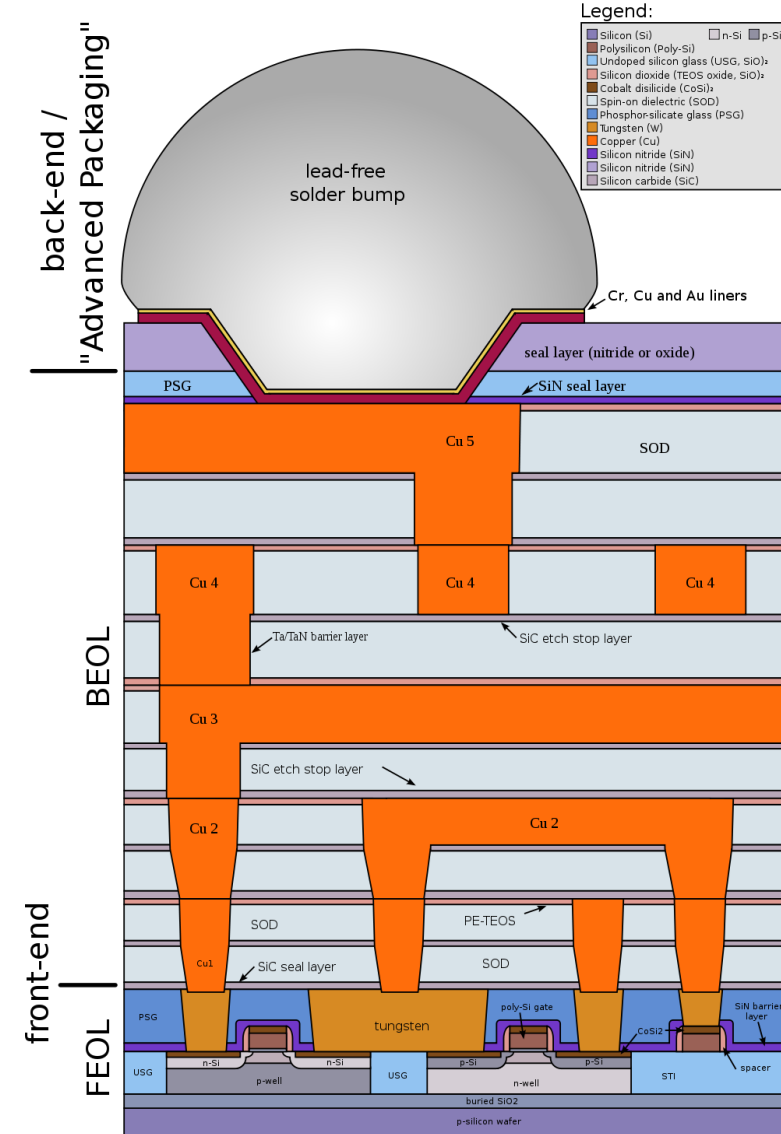


0.5mm



1. Grow field oxide
ox.
p-type substrate
2. Etch oxide for pMOSFET
ox.
p-type substrate
3. Diffuse n-well
ox.
p-type substrate n-well
4. Etch oxide for nMOSFET
ox.
p-type substrate n-well
5. Grow gate oxide
ox.
p-type substrate n-well
6. Deposit polysilicon
ox.
p-type substrate n-well
7. Etch polysilicon and oxide
ox.
p-type substrate n-well
8. Implant sources and drains
ox.
p-type substrate n-well
9. Grow nitride
ox.
p-type substrate n-well
10. Etch nitride
ox.
p-type substrate n-well
11. Deposit metal
ox.
p-type substrate n-well
12. Etch metal
ox.
p-type substrate n-well

Simplified process of fabrication of a CMOS inverter on p-type substrate in semiconductor microfabrication



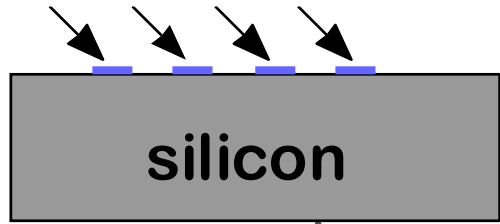


Processing Using Diffusion

Doping Silicon with P for n-type semiconductors:

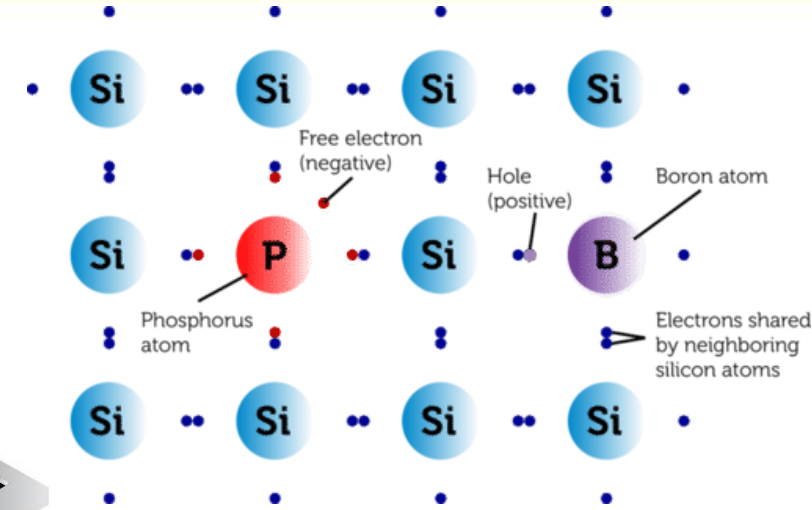
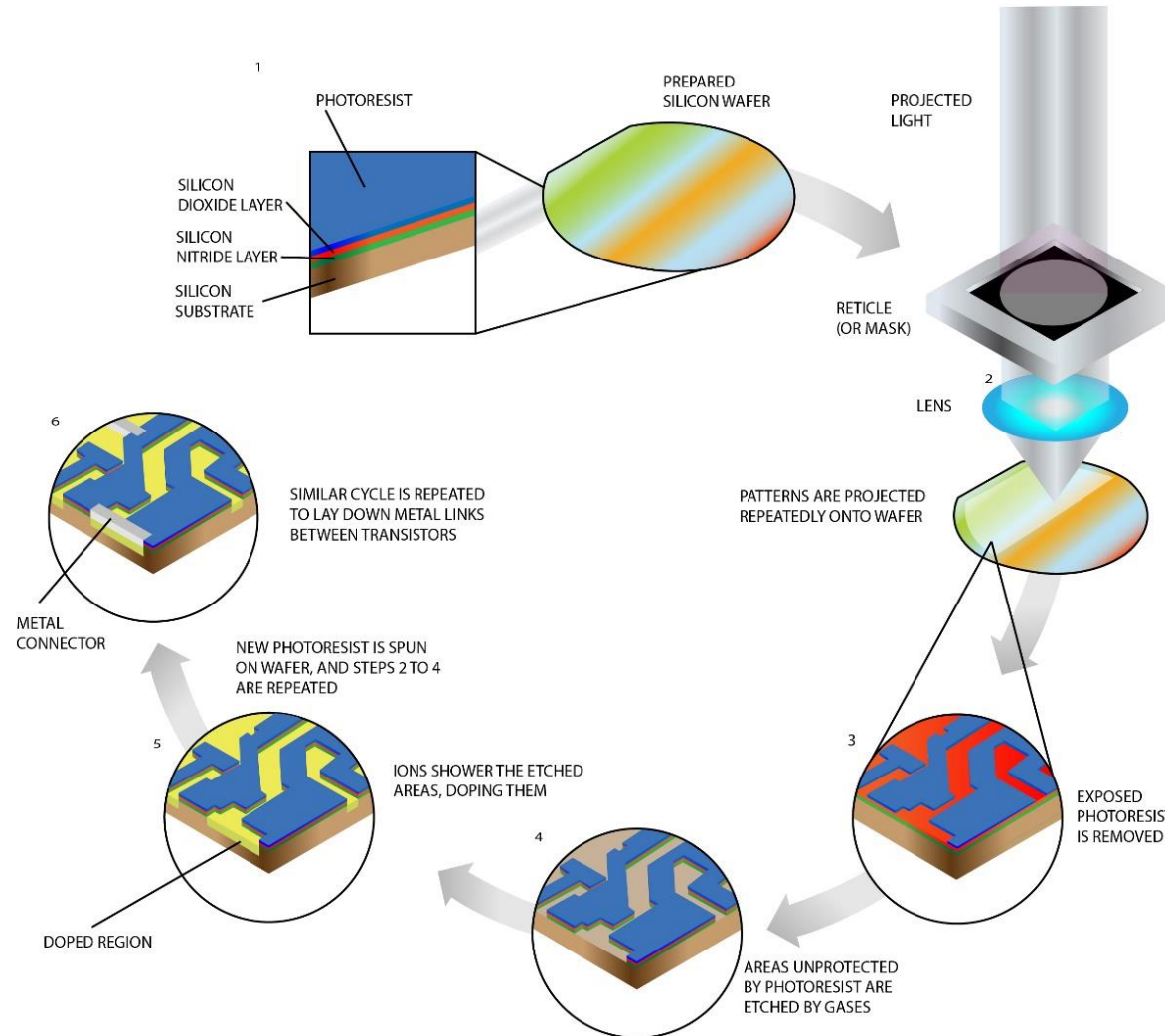
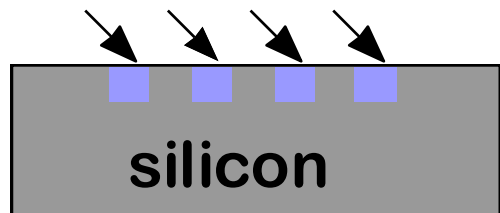
Process:

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



2. Heat it.

3. Result: Doped semiconductor regions.





Diffusion Flux : Fick's First Law

Diffusion is a *time-dependent process*

Diffusion flux (J), defined as the mass (or, equivalently, the number of atoms) M diffusing through and perpendicular to a unit cross-sectional area of solid per unit of time.

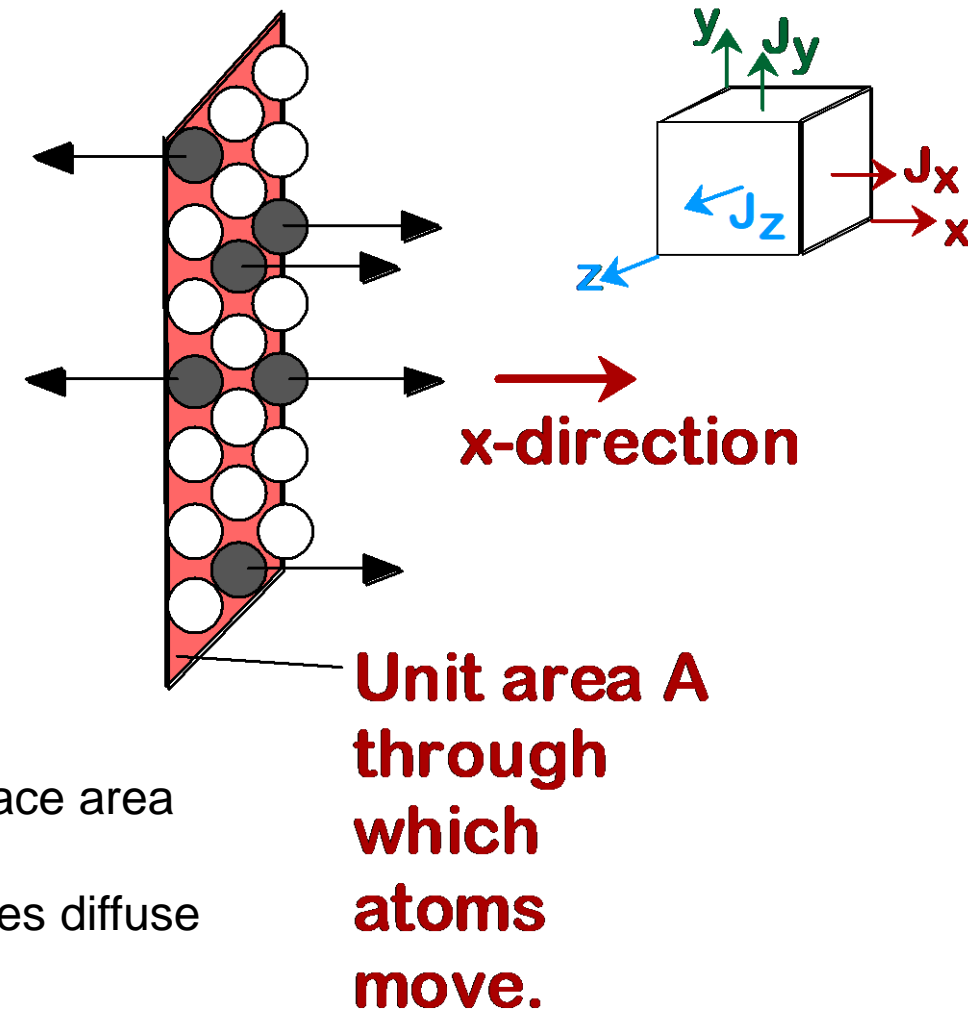
$$J = \frac{1}{A} \frac{dM}{dt} \Rightarrow \left[\frac{\text{kg}}{\text{m}^2\text{s}} \right] \text{ or } \left[\frac{\text{atoms}}{\text{m}^2\text{s}} \right]$$

- Directional Quantity

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

- **Empirically determined:**

- Make thin membrane of known surface area
- Impose concentration gradient
- Measure how fast atoms or molecules diffuse through the membrane

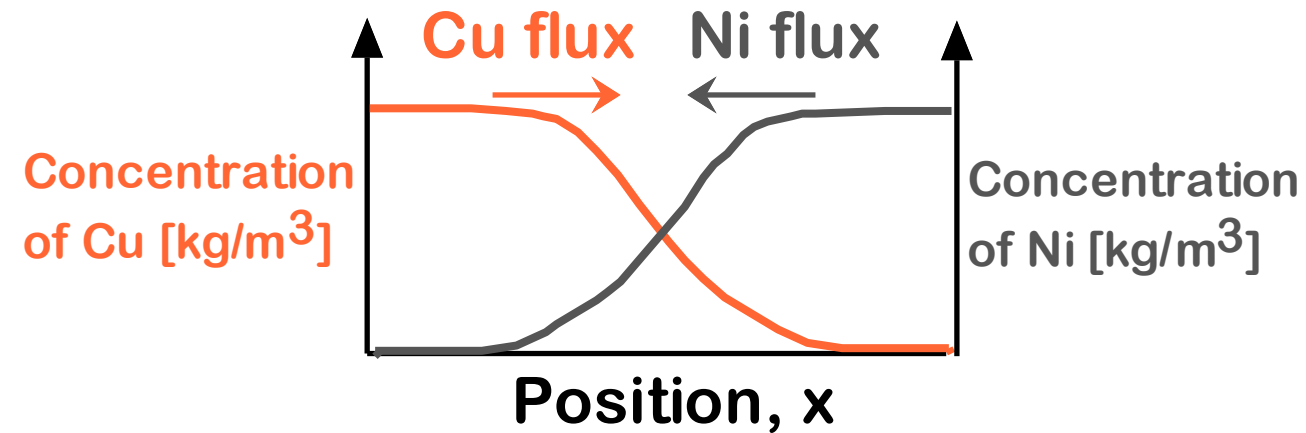




Concentration Profiles & Flux

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

The mathematics of steady-state diffusion in a single (x) direction is relatively simple, in that the flux is proportional to the concentration gradient



- **Fick's First Law:** D is a constant!

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

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

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

- The steeper the concentration profile, the greater the flux!
- The minus sign in the equation means that diffusion is down the concentration gradient, from a high to a low concentration
i.e., the negative sign cancels the negative gradient along the direction of positive flux..





Steady State Diffusion

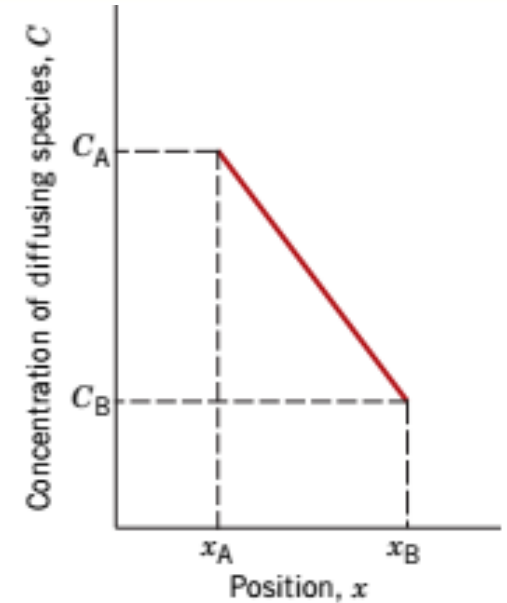
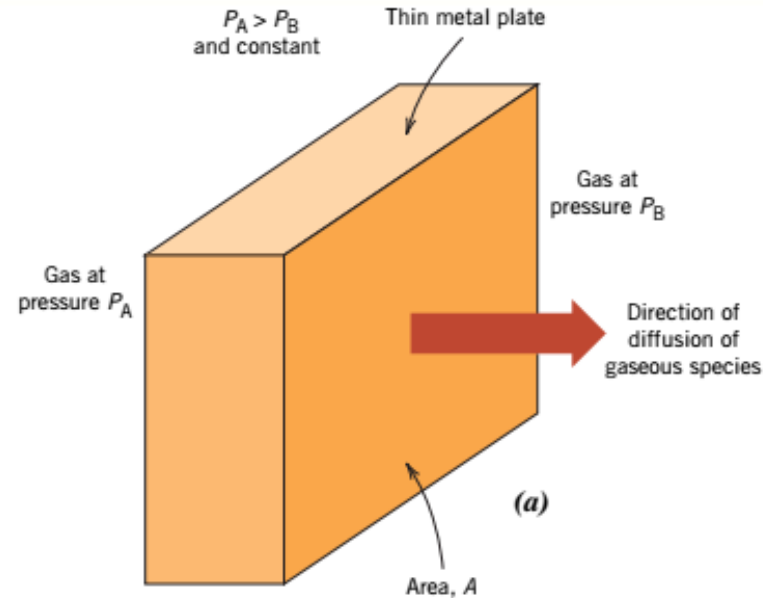
- **Steady State:** the concentration profile doesn't change with time.

- **Apply Fick's First Law:**
the diffusion flux along direction x is proportional to the concentration gradient

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

- If $J_{x\text{left}} = J_{x\text{right}}$, then $\left(\frac{dC}{dx}\right)_{\text{left}} = \left(\frac{dC}{dx}\right)_{\text{right}}$

- Result: the slope, dC/dx , must be constant (i.e., slope doesn't vary with position)!



- When concentration C is plotted versus position (or distance) within the solid x , the resulting curve is termed the **concentration profile**
- **concentration gradient** is the slope at a particular point on this curve.

$$\text{concentration gradient} = \frac{dC}{dx} = \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$$

The concentration gradient is often called the *driving force* in diffusion (but it is not a force in the mechanistic sense).

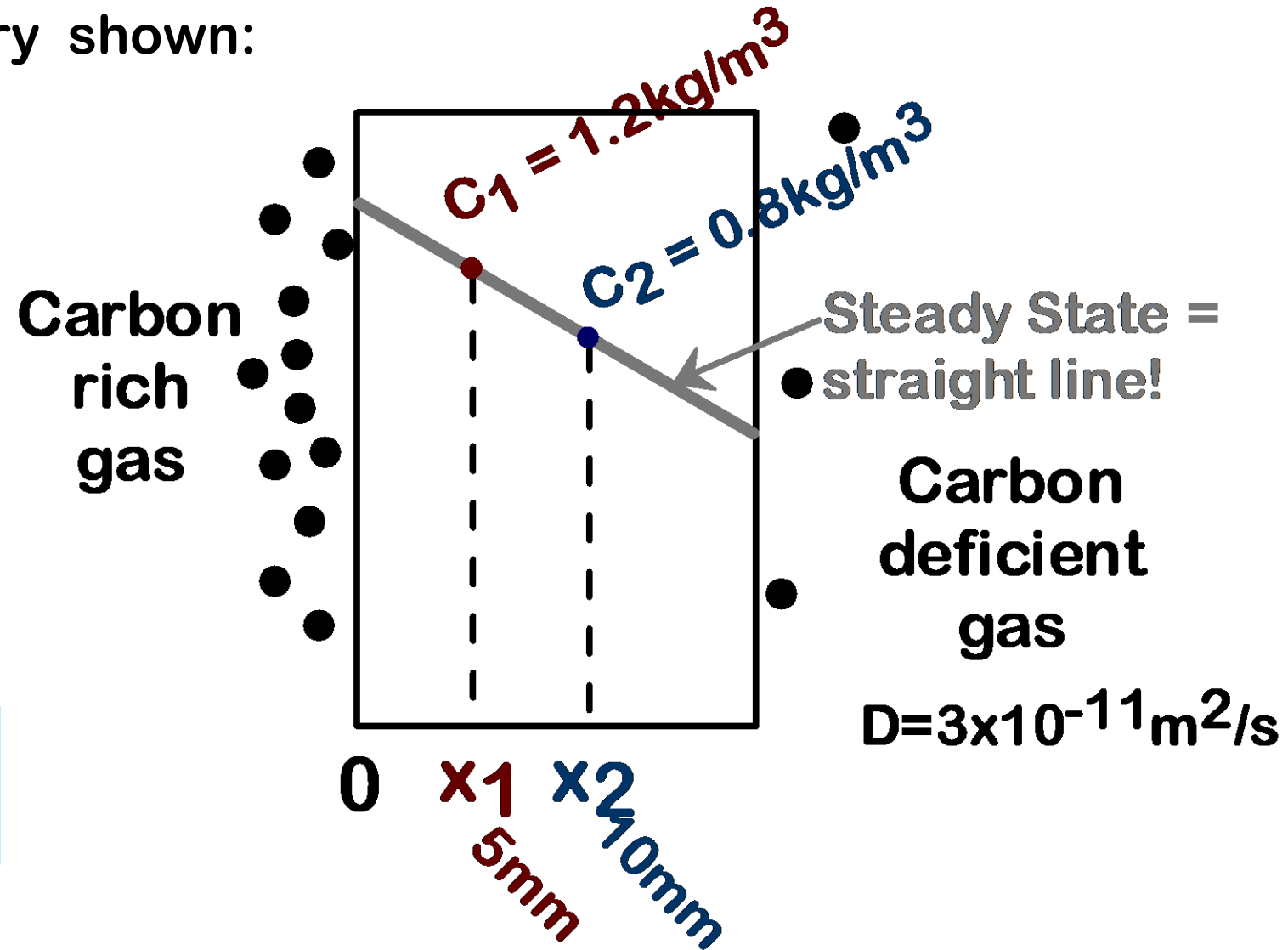


Ex: Steady State Diffusion

Steel plate at 700C with geometry shown:

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

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





Where can we use Fick's Law?

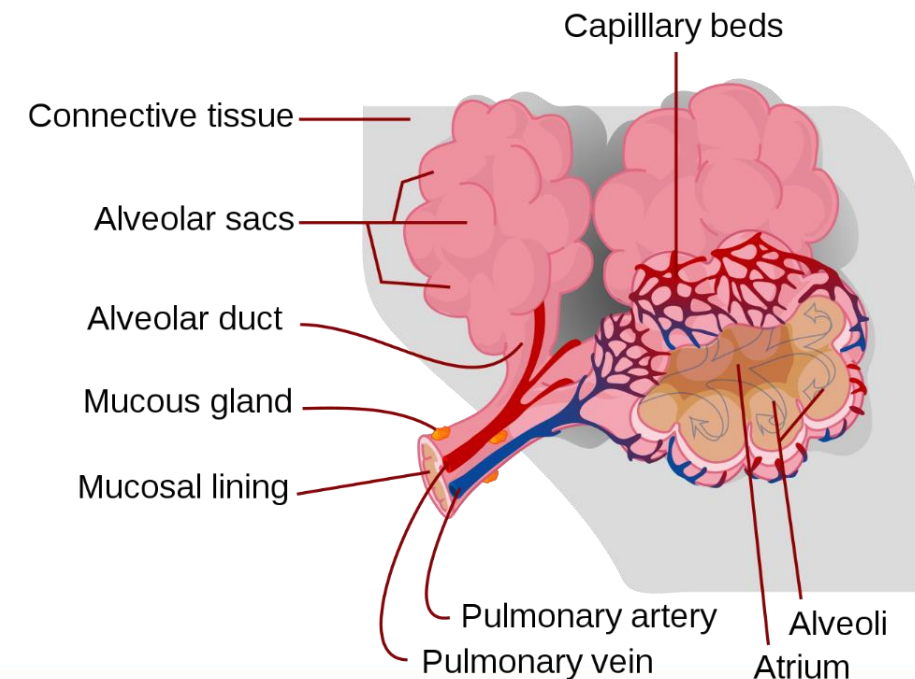
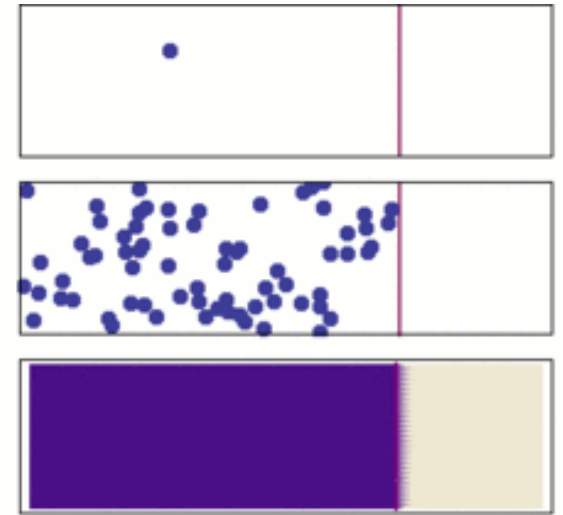
Fick's law is commonly used to model transport processes in

- foods,
- clothing,
- biopolymers,
- pharmaceuticals,
- porous soils,
- semiconductor doping process, etc.

Example

The total membrane surface area in the lungs (alveoli) may be on the order of 100 square meters and have a thickness of less than a millionth of a meter, so it is a very effective gas-exchange interface.

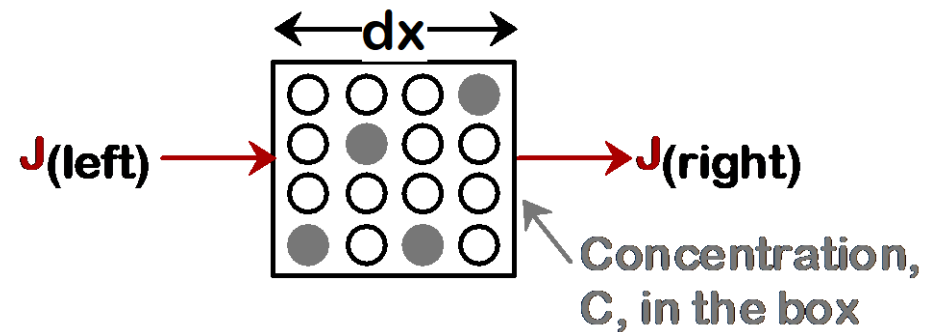
CO₂ in air has $D \sim 16 \text{ mm}^2/\text{s}$, and, in water, $D \sim 0.0016 \text{ mm}^2/\text{s}$





Non-steady-State Diffusion: Fick's second law

In many real situations the concentration $C(x)$ profile and the concentration gradient are changing with time. The changes of the concentration profile can be described in this case by a differential equation, **Fick's second law**.



- To conserve matter:

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

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

equate

$$\frac{dJ}{dx} = -D \frac{d^2C}{dx^2}$$

- Fick's First Law:

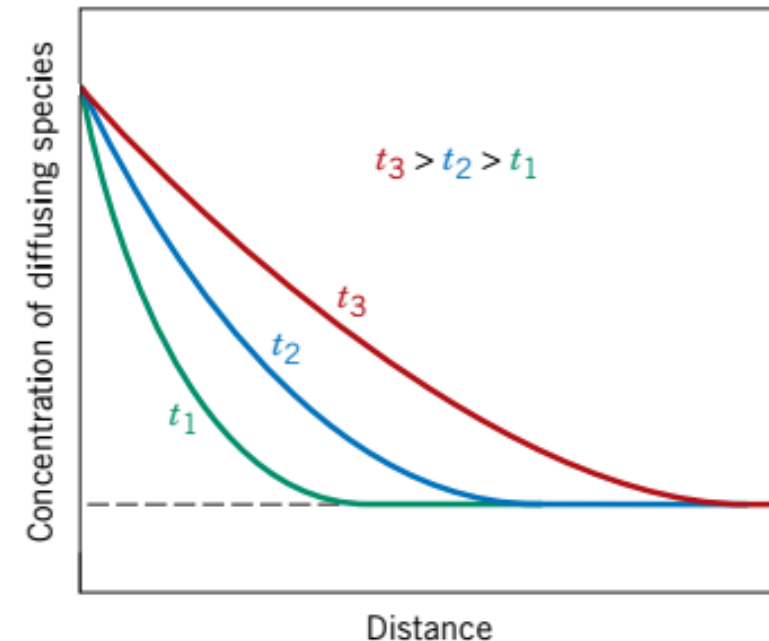
$$J = -D \frac{dC}{dx}$$

if D does not depend on x

if D is constant

Ficks Second Law:

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





Solution to Fick's second law

Boundary Condition: a semi-infinite solid in which the surface concentration is held constant

A bar of length l is considered to be semi-infinite when $l > 10\sqrt{Dt}$.

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

1. Before diffusion, any of the diffusing solute atoms in the solid are uniformly distributed with concentration of C_0 .
2. The value of x at the surface is zero and increases with distance into the solid.
3. The time is taken to be zero the instant before the diffusion process begins.

These conditions are simply stated as follows:

Initial condition

$$\text{For } t = 0, C = C_0 \text{ at } 0 \leq x \leq \infty$$

Boundary conditions

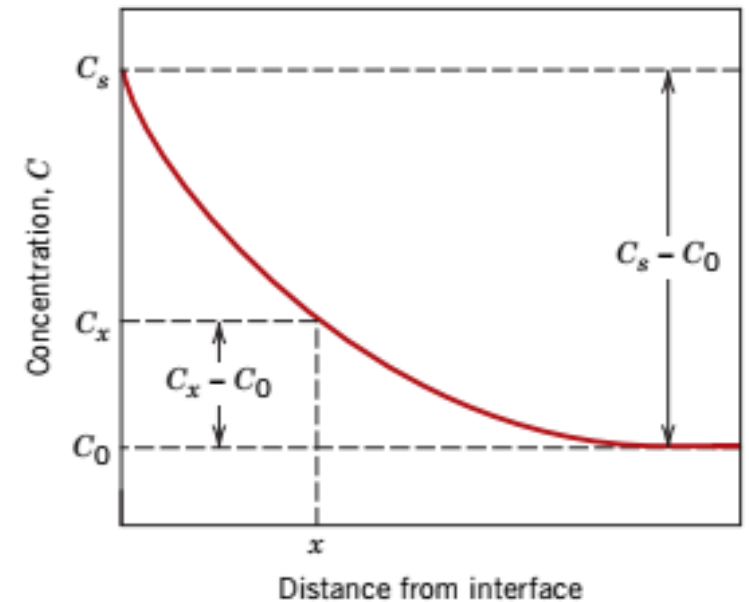
$$\text{For } t > 0, C = C_s \text{ (the constant surface concentration) at } x = 0$$

$$\text{For } t > 0, C = C_0 \text{ at } x = \infty$$

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

C_x represents the concentration at depth x after time t .

"error function" $\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy$



Suppose that it is desired to achieve some specific concentration of solute, C_1 , in an alloy;

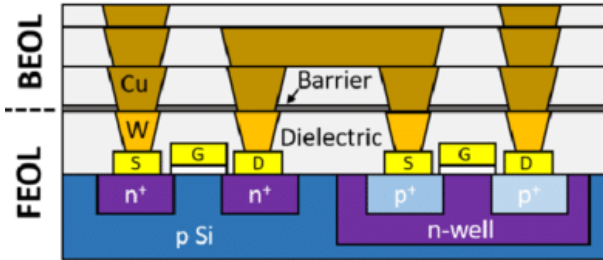
$$\frac{C_1 - C_0}{C_s - C_0} = \text{constant} \quad \Rightarrow \quad \frac{x}{2\sqrt{Dt}} = \text{constant}$$

$$\frac{x^2}{Dt} = \text{constant}$$



DIFFUSION IN SEMICONDUCTING MATERIALS: Fick's second law

a, Si CMOS chip



The solution to Fick's second law for drive-in diffusion takes the form

$$C(x,t) = \frac{Q_0}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

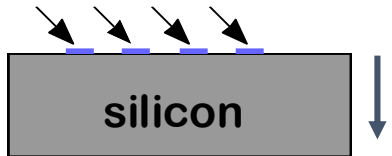
Q_0 represents the total amount of impurities in the solid that were introduced during the predeposition treatment

$$Q_0 = 2C_s \sqrt{\frac{D_p t_p}{\pi}}$$

where C_s is the surface concentration for the predeposition step, which was held constant, D_p is the diffusion coefficient, and t_p is the predeposition treatment time

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

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



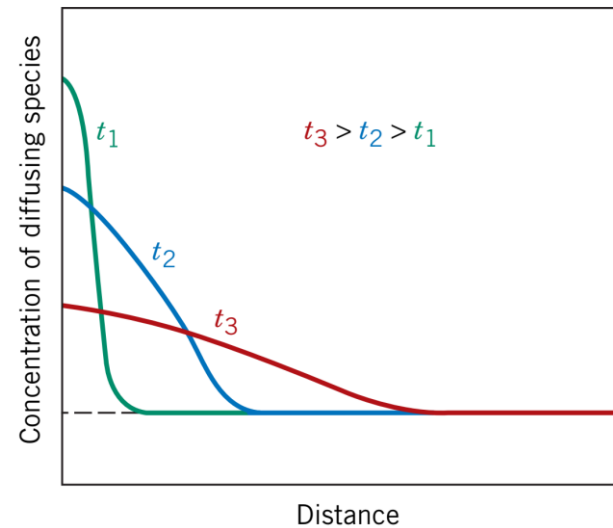
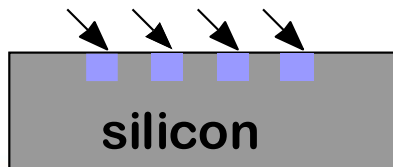
Predeposition step, impurity atoms are diffused into the silicon, often from a gas phase, the partial pressure of which is maintained constant. The surface composition of the impurity also remains constant over time, such that impurity concentration within the silicon is a function of position and time according

2. **Heat it**

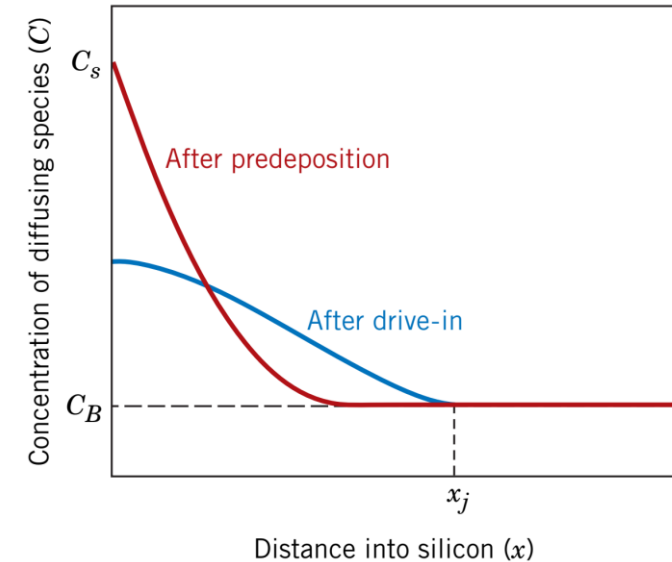
(900°C and 1000°C, <1 h)

3. **Drive-in diffusion** is used to transport impurity atoms farther into the silicon

(up to about 1200°C)



Schematic concentration profiles for drive-in diffusion of semiconductors at three different times, t_1 , t_2 , and t_3 .



Schematic concentration profiles taken after (1) predeposition and (2) drive-in diffusion treatments for semiconductors. Also shown is the junction depth, x_j .



Tabulation of Error Function Values

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

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

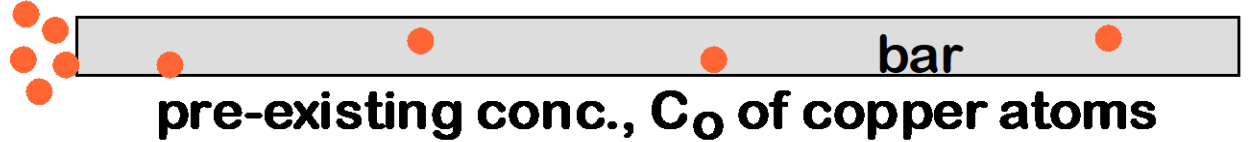




Ex: Non Steady State Diffusion

Copper diffuses into a bar of aluminum.

Surface conc.,
 C_s of Cu atoms



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

Key point 1: $C(x, t_{500C}) = C(x, t_{600C})$.

Key point 2: Both cases have the same C_0 and C_s .

- Result: Dt should be held constant.

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

- Answer:

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

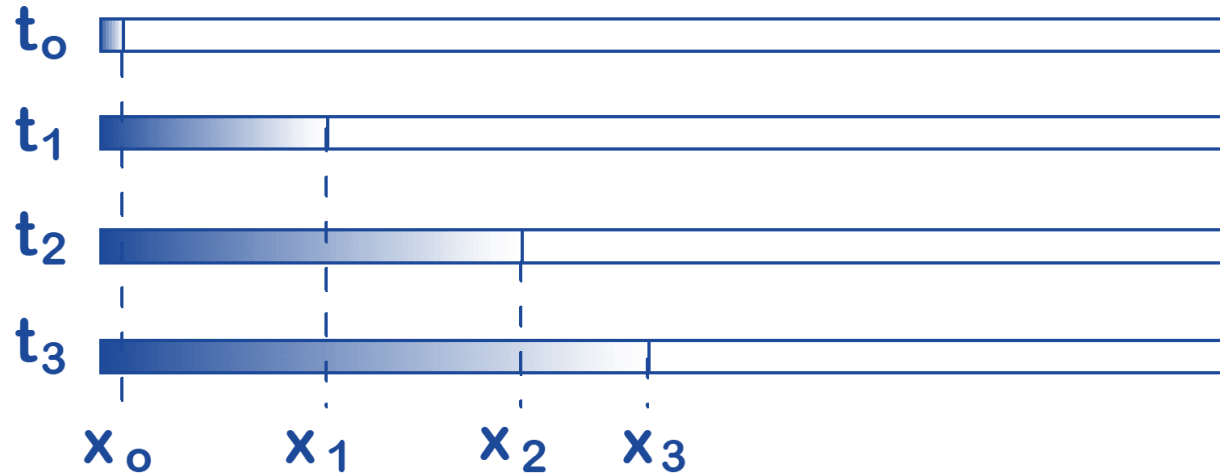
$5.3 \times 10^{-13} \text{m}^2/\text{s}$ (points to $(Dt)_{600}$)
 10hrs (points to $(Dt)_{600}$)
 $4.8 \times 10^{-14} \text{m}^2/\text{s}$ (points to D_{500})

Note: values of D are provided here



Diffusion Analysis

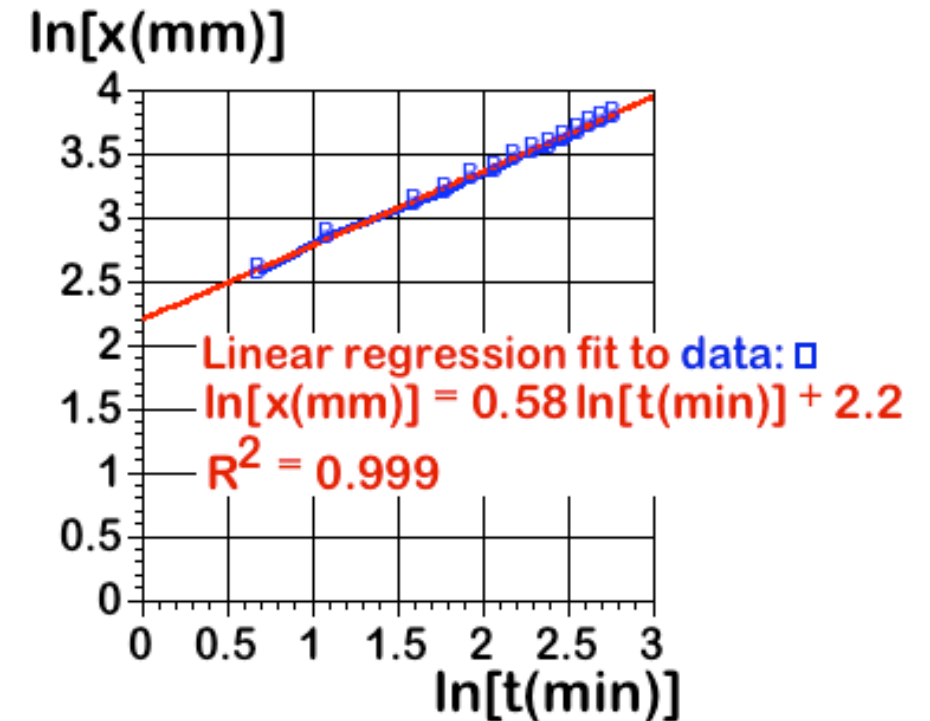
- The experiment: recorded combinations of t and x that kept C constant.



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

- Diffusion depth given by: $x_i \propto \sqrt{Dt_i}$

Data from Diffusion Analysis



- Experimental result: $x \sim t^{0.58}$
- Theory predicts $x \sim t^{0.50}$ from
- Close agreement.

$$x_i \propto \sqrt{Dt_i}$$



Factors that influence diffusion

- **Temperature** - diffusion rate increases very rapidly with increasing temperature
- **Diffusion mechanism** – diffusion by interstitial mechanism is usually faster than by vacancy mechanism
- **Diffusing and host species** - D_o , Q_d are different for every solute, solvent pair
- **Microstructure** - diffusion is faster in polycrystalline materials compared to single crystals because of the accelerated diffusion along grain boundaries.



Factors That Influence Diffusion : **Temperature**

Diffusivity increases with T (so does Vacancy conc.)

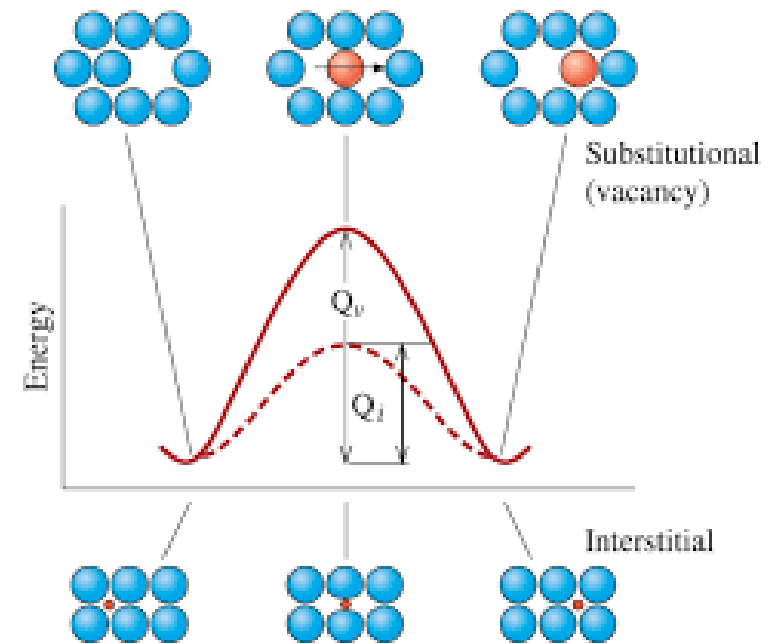
$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

D_0 – temperature-independent pre-exponential (m^2/s)

Q_d – the activation energy for diffusion (J/mol or eV/atom)

R – the gas constant (8.31 J/mol-K or $8.62 \times 10^{-5} \text{ eV/atom-K}$)

T – absolute temperature (K)



The above equation can be rewritten as

$$\ln D = \ln D_0 - \frac{Q_d}{R} \left(\frac{1}{T} \right) \quad \text{or} \quad \log D = \log D_0 - \frac{Q_d}{2.3R} \left(\frac{1}{T} \right)$$

The activation energy Q_d and pre-exponential D_0 , therefore, can be estimated by plotting $\ln D$ versus $1/T$ or $\log D$ versus $1/T$. Such plots are called Arrhenius plots.

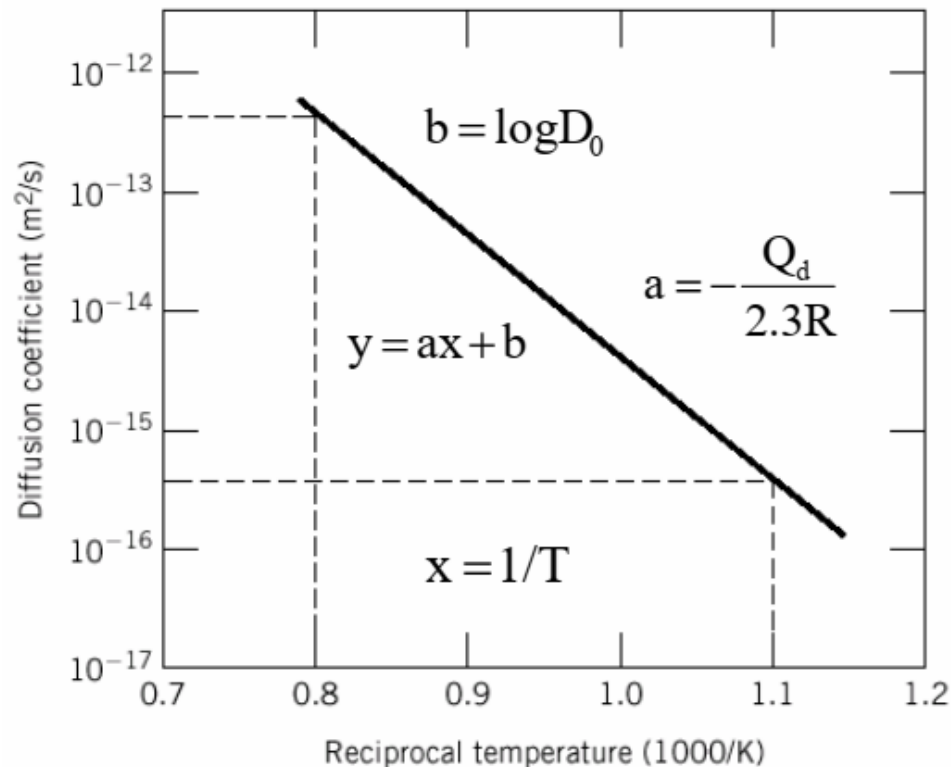




Diffusion – Temperature Dependence

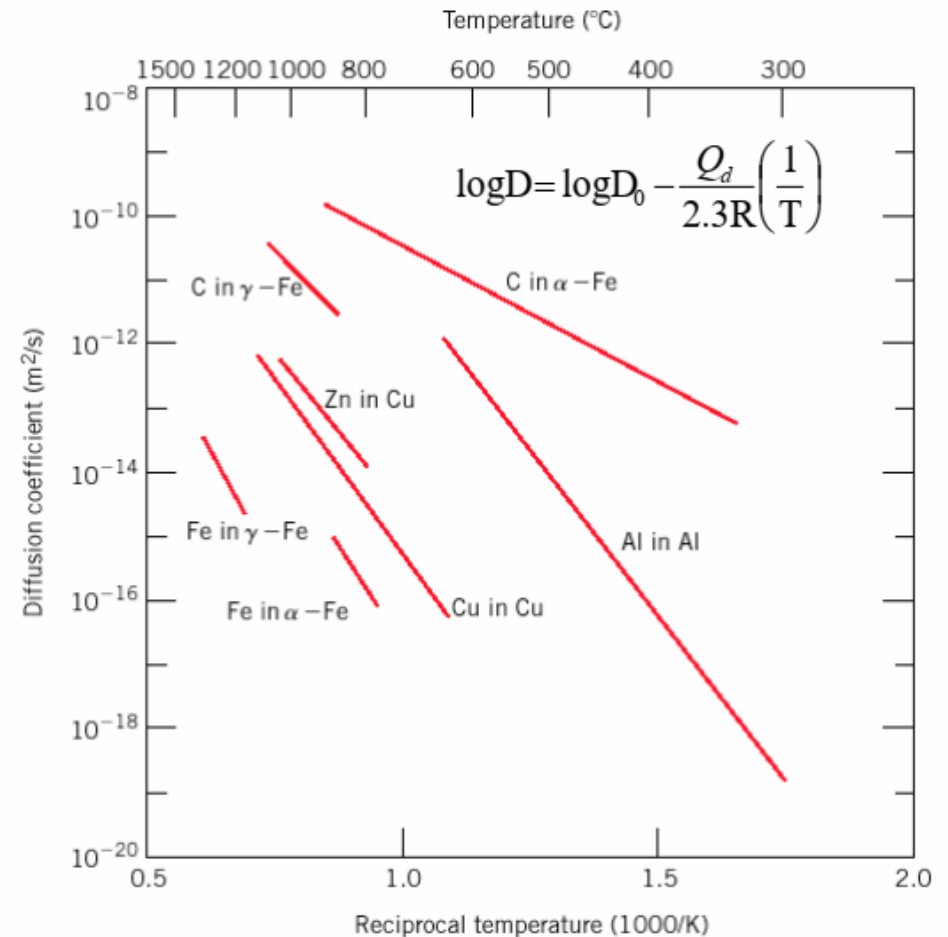
$$\log D = \log D_0 - \frac{Q_d}{2.3R} \left(\frac{1}{T} \right)$$

$$Q_d = -2.3R \left[\frac{\log D_1 - \log D_2}{1/T_1 - 1/T_2} \right]$$



Graph of $\log D$ vs. $1/T$ has slope of $-Q_d/2.3R$, intercept of $\log D_0$

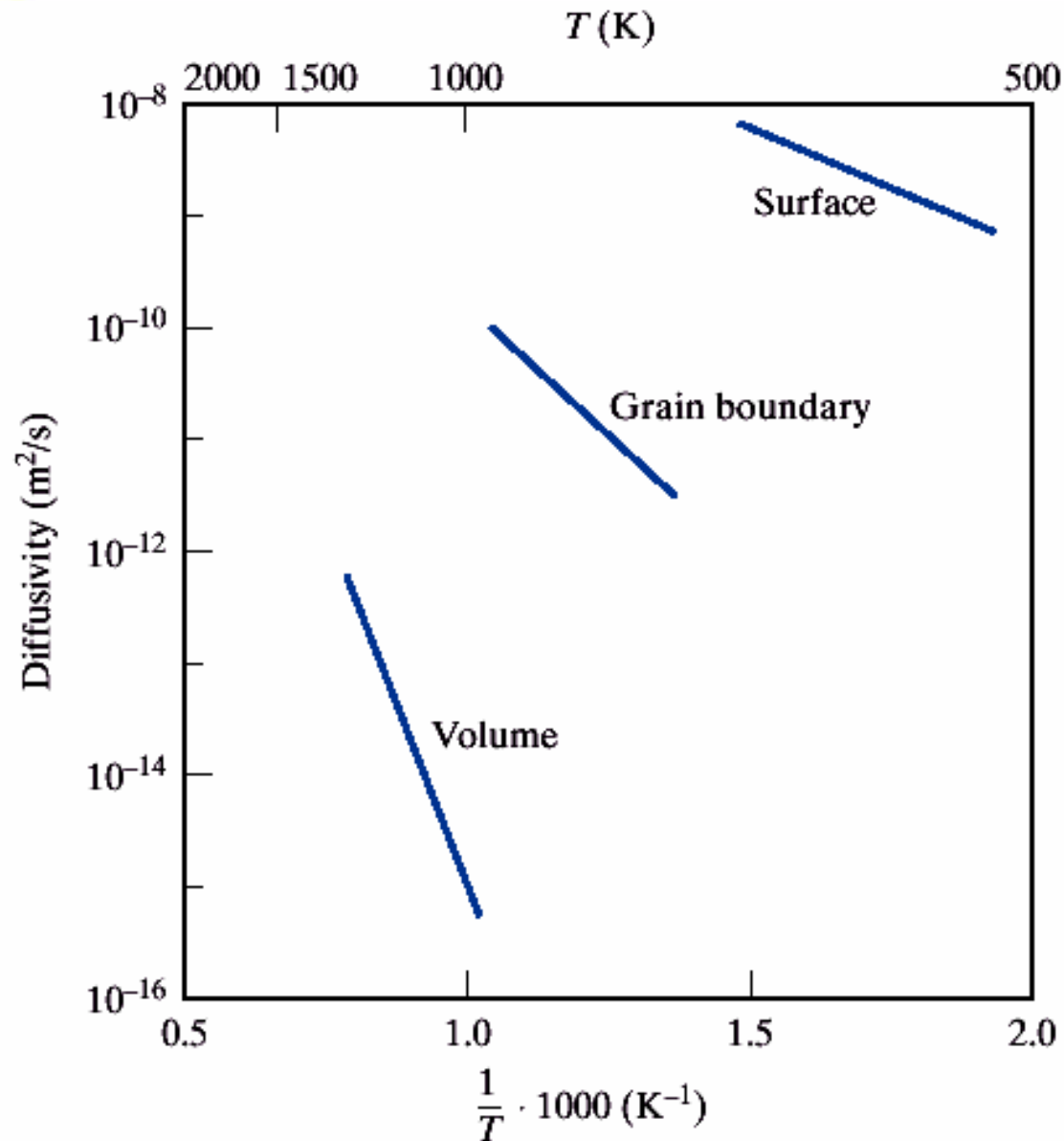
Interstitial and vacancy



Diffusion of interstitials is typically faster as compared to the vacancy diffusion mechanism (self-diffusion or diffusion of substitutional atoms)



Diffusion: Role of the microstructure



Self-diffusion coefficients for Ag depend on the diffusion path.

In general the diffusivity is greater through less restrictive structural regions – grain boundaries, dislocation cores, external surfaces.





Diffusion In Polymeric Materials

- Interest is the diffusive motion of small foreign molecules (e.g., O_2 , H_2O , CO_2 , CH_4) between the molecular chains rather than in the diffusive motion of chain atoms within the polymer structure
- A polymer's permeability and absorption characteristics relate to the degree to which foreign substances diffuse into the material.

Diffusion properties of polymers are often characterized in terms of a **permeability coefficient** (denoted by P_M), where for the case of steady-state diffusion through a polymer membrane, Fick's first law is modified as

$$J = -P_M \frac{\Delta P}{\Delta x}$$

J is the diffusion flux of gas through the membrane $[(cm^3STP)/(cm^2 \cdot s)]$,
 P_M is the permeability coefficient, Δx is the membrane thickness,
 ΔP is the difference in pressure of the gas across the membrane

For small molecules in nonglossy polymers the permeability coefficient can be approximated as the product of the diffusion coefficient (D) and solubility of the diffusing species in the polymer (S)

$$P_M = DS$$

When the diffusing molecular species is in the gas phase, solubility is equal to **$S = C/P$**

C is the concentration of the diffusing species in the polymer

Permeability Coefficient P_M at 25°C for Oxygen, Nitrogen, Carbon Dioxide, and Water Vapor in a Variety of Polymers

Polymer	Acronym	P_M [$\times 10^{-13} (cm^3 STP)(cm)/(cm^2 \cdot s \cdot Pa)$]			
		O_2	N_2	CO_2	H_2O
Polyethylene (low density)	LDPE	2.2	0.73	9.5	68
Polyethylene (high density)	HDPE	0.30	0.11	0.27	9.0
Polypropylene	PP	1.2	0.22	5.4	38
Poly(vinyl chloride)	PVC	0.034	0.0089	0.012	206
Polystyrene	PS	2.0	0.59	7.9	840
Poly(vinylidene chloride)	PVDC	0.0025	0.00044	0.015	7.0
Poly(ethylene terephthalate)	PET	0.044	0.011	0.23	—
Poly(ethyl methacrylate)	PEMA	0.89	0.17	3.8	2380



Other Types of Diffusion besides atomic....

• Charge Flux –

$$j_q = \frac{1}{A} \frac{dq}{dt} = \frac{1}{A} \frac{d(Ne)}{dt}$$

e = electric charge

N = Number of e⁻ cross area A

Defining conductivity σ
(a material property)

$$j = -\sigma \frac{dV}{dx}$$

Ohm's Law $j_q = \frac{I}{A} = \frac{1}{A} \frac{V}{R} = \sigma \frac{V}{\ell}$

Solution: Fick's 2nd Law

$$\frac{V_x - V_s}{V_0 - V_s} = \text{erf} \left(\frac{x}{2\sqrt{\sigma t}} \right)$$

• Heat Flux – (by phonons)

$$Q = \frac{1}{A} \frac{dH}{dt} = \frac{1}{A} \frac{d(N\varepsilon)}{dt}$$

N = Number of phonon with average energy ε

Defining thermal conductivity κ
(a material property)

$$Q = -\kappa \frac{dT}{dx}$$

Solution: Fick's 2nd Law

$$\frac{T_x - T_s}{T_0 - T_s} = \text{erf} \left(\frac{x}{2\sqrt{ht}} \right)$$

Or w/ Thermal Diffusivity: $h = \frac{\kappa}{c_v \rho} \quad Q = c_v \rho T$





Ionic Conduction: related to fuel cells

Molten salts and aqueous electrolytes conduct charge when placed in electric field, +q and -q move in opposite directions.

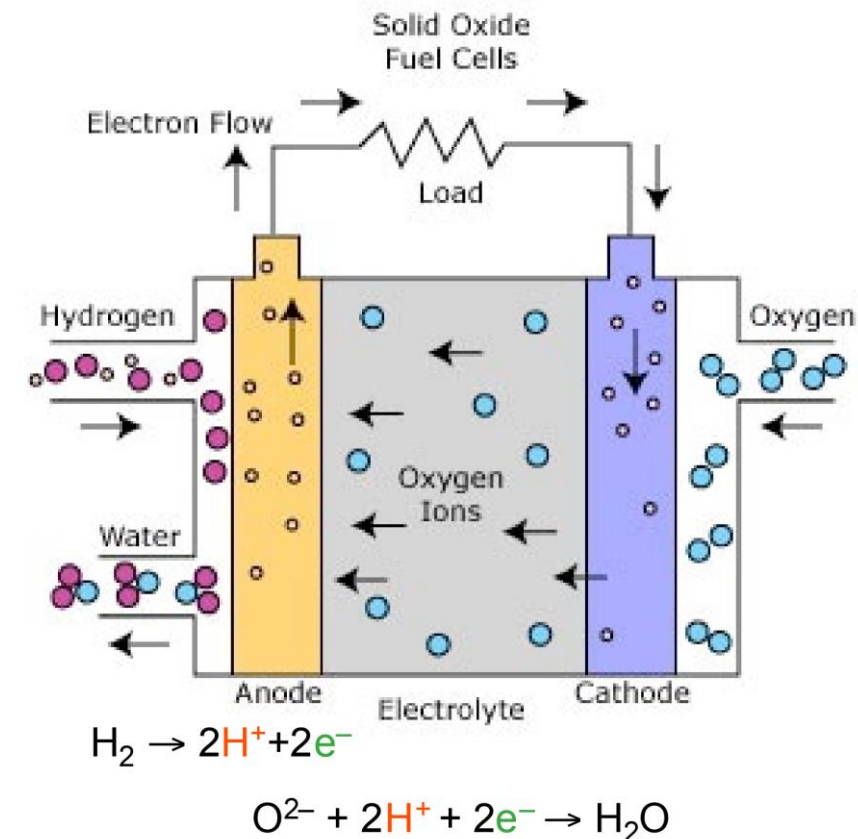
The same occurs in solids although at much slower rate.

- Each ion has **charge of Ze** ($e = 1.6 \times 10^{-19}$ amp*sec),
so ion movement induces ionic conduction
- **Conductivity** $\sigma = n\mu Ze$ is related to **mobility, μ** ,
related to D via the Einstein equations: $\mu = ZeD / k_B T$

$$\sigma_{ionic} = \frac{nZ^2 e^2}{k_B T} D = \frac{nZ^2 e^2}{k_B T} D_o e^{-Q/RT}$$

$$\log_{10} \sigma_{ionic} \sim \ln \left(\frac{nZ^2 e^2}{k_B T} D_o \right) - \frac{Q}{2.3RT}$$

Example: solid-oxide fuel cell (SOFC)





Summary: Structure & Diffusion

Diffusion **FASTER** for...

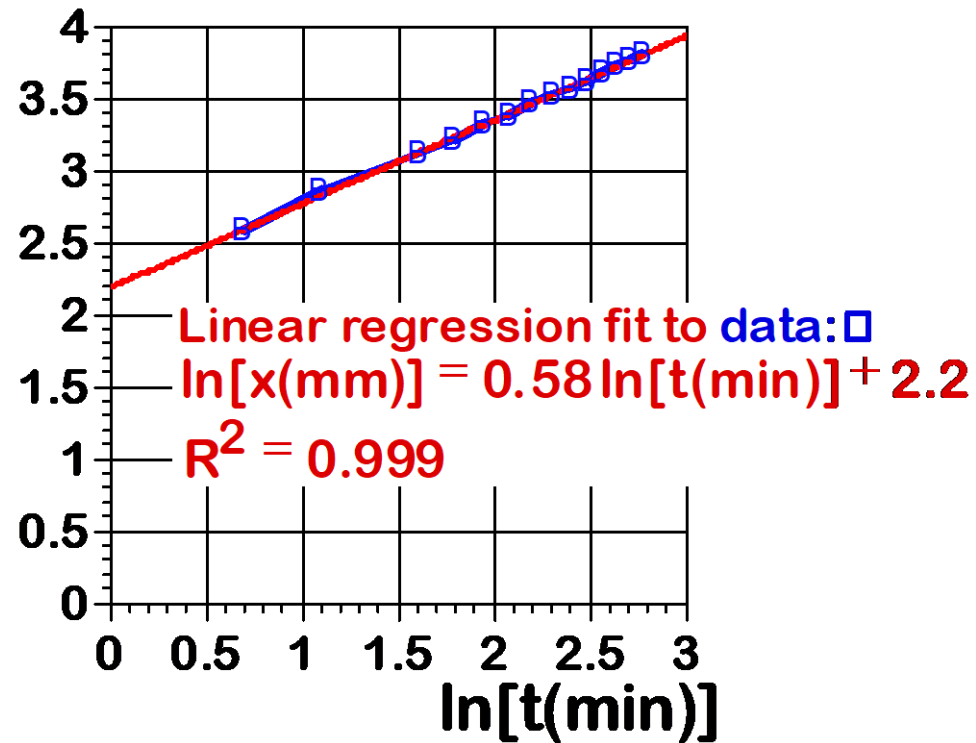
- open crystal structures
- lower melting T materials
- materials w/secondary bonding
- smaller diffusing atoms
- cations
- lower density materials

Diffusion **SLOWER** for...

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



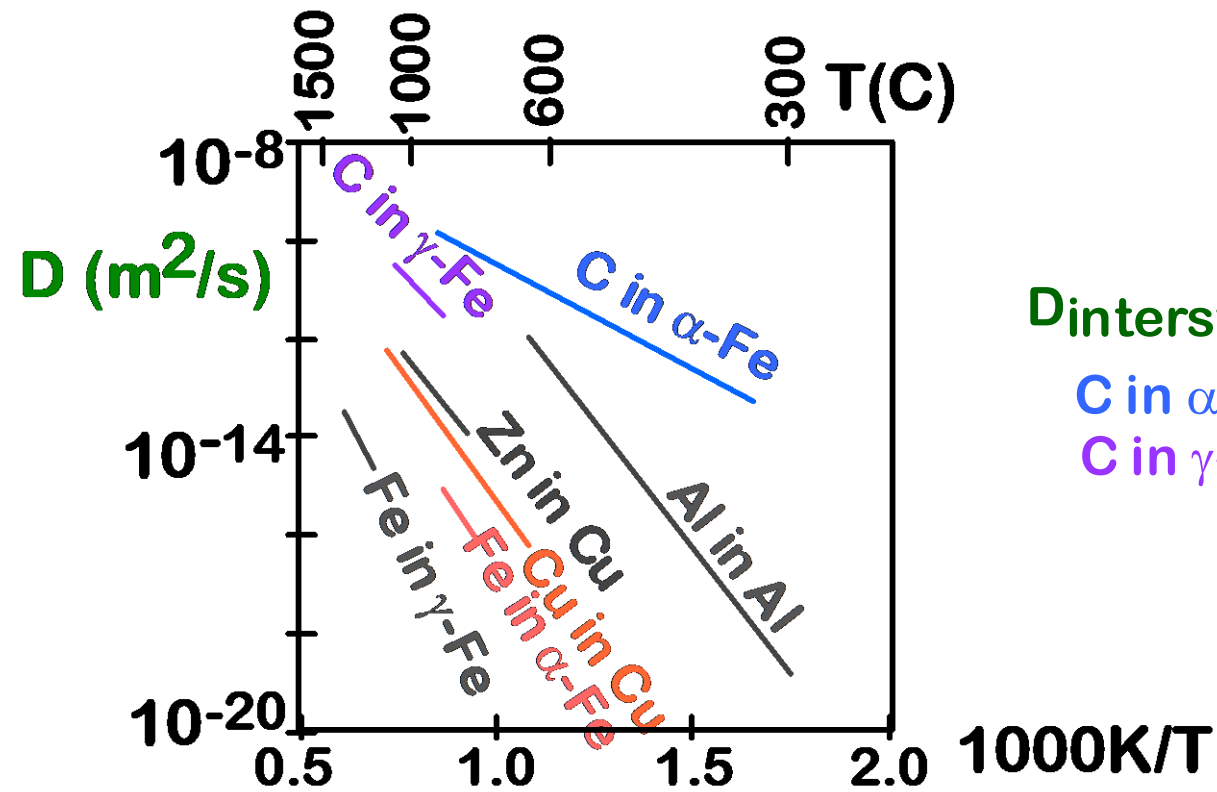
Data From Diffusion Demo



- Experimental result: $x \sim t^{0.58}$
- Theory predicts $x \sim t^{0.50}$
- Reasonable agreement!



Experimental Data:



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

$\text{C in } \alpha\text{-Fe}$
 $\text{C in } \gamma\text{-Fe}$

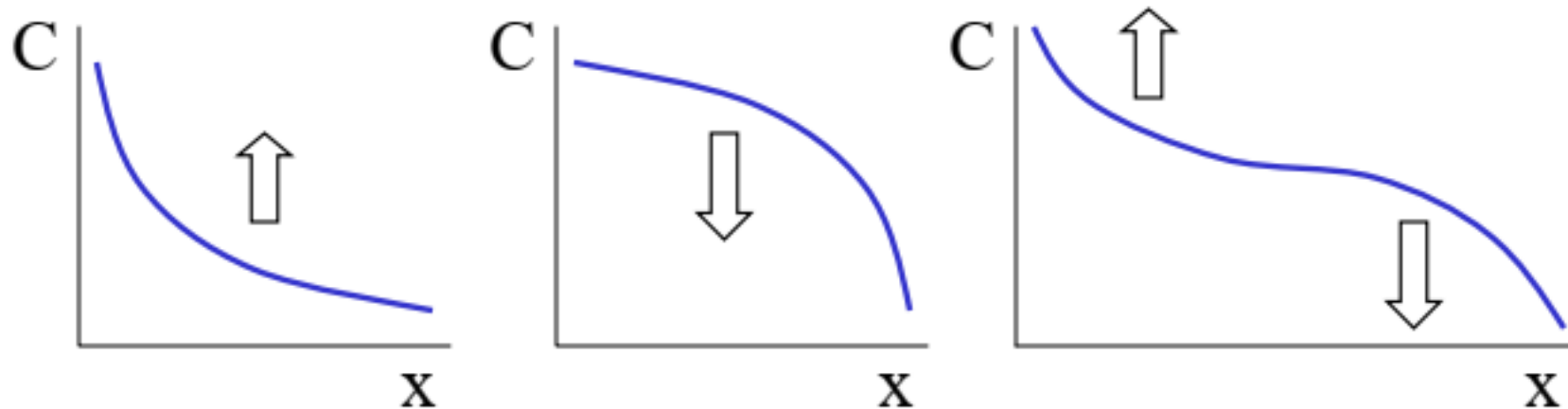
Cu in Cu
 Al in Al
 $\text{Fe in } \alpha\text{-Fe}$
 $\text{Fe in } \gamma\text{-Fe}$
 Zn in Cu



Nonsteady-State Diffusion: Fick's second law

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

Fick's second law relates the rate of change of composition with time to the curvature of the concentration profile:



- Concentration increases with time in those parts of the system where concentration profile has a positive curvature. And decreases where curvature is negative.
- The phenomenological description based on the Fick's laws is valid for any atomic mechanism of diffusion. Understanding of the atomic mechanisms is important, however, for predicting the dependence of the atomic mobility (and, therefore, diffusion coefficient) on the type of interatomic bonding, temperature, and microstructure.

