Chapter 5

Diffusion (Atom/Ion/Molecule Movement in Materials)

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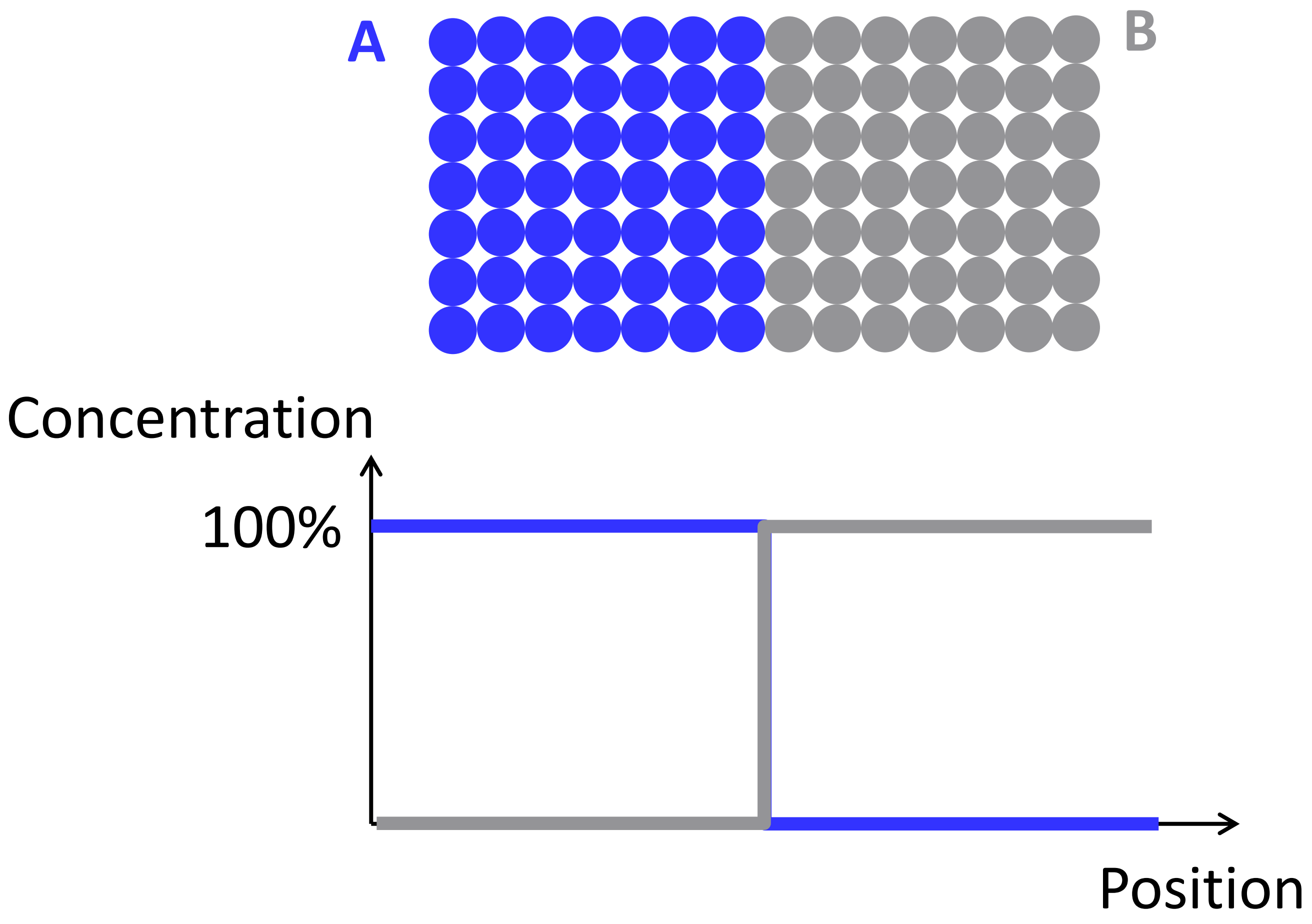
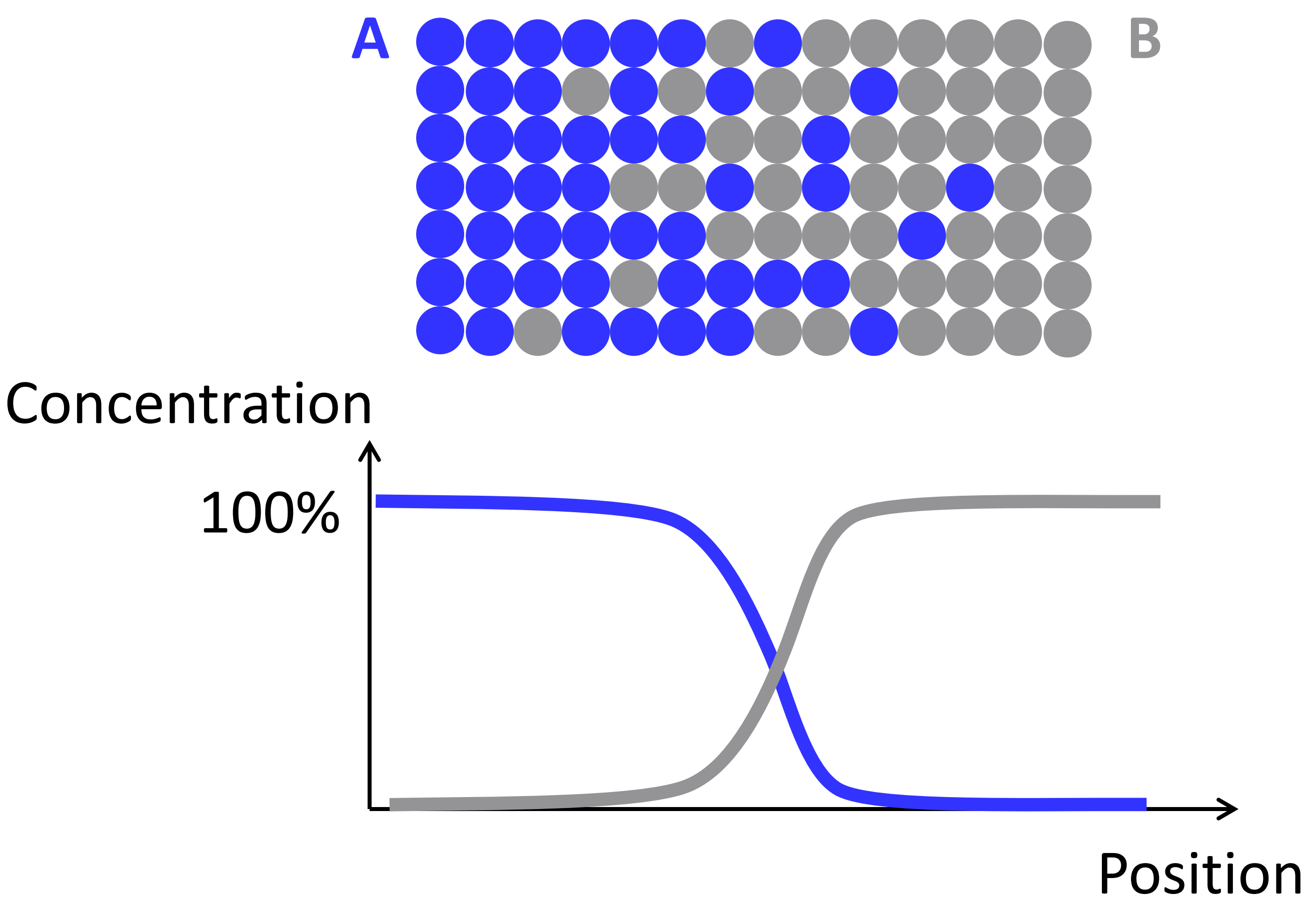
Diffusion

- **Definition**: Mass transport (in solid, liquid, or gas) by **random**, atomic (or molecular-scale) motion
- Often from regions of high concentration to low concentration - **interdiffusion**



Initial

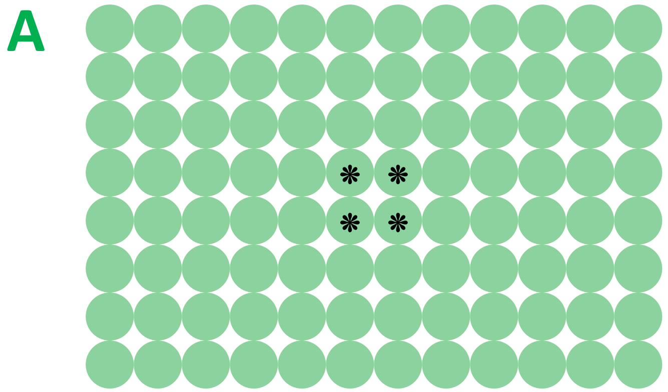


After a while

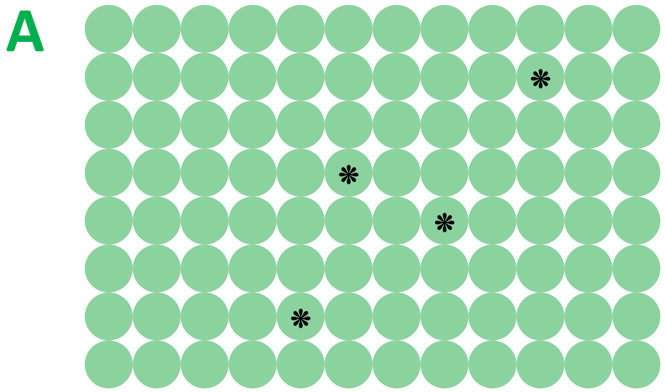
Self Diffusion

- Even in a pure elemental solid (i.e., no chemical concentration difference), atoms do NOT sit still - they move randomly via self-diffusion process

Locally implant radio active isotope *A



Track spread of radio active isotope *A over time



Examples of Diffusion & Inhibiting Diffusion

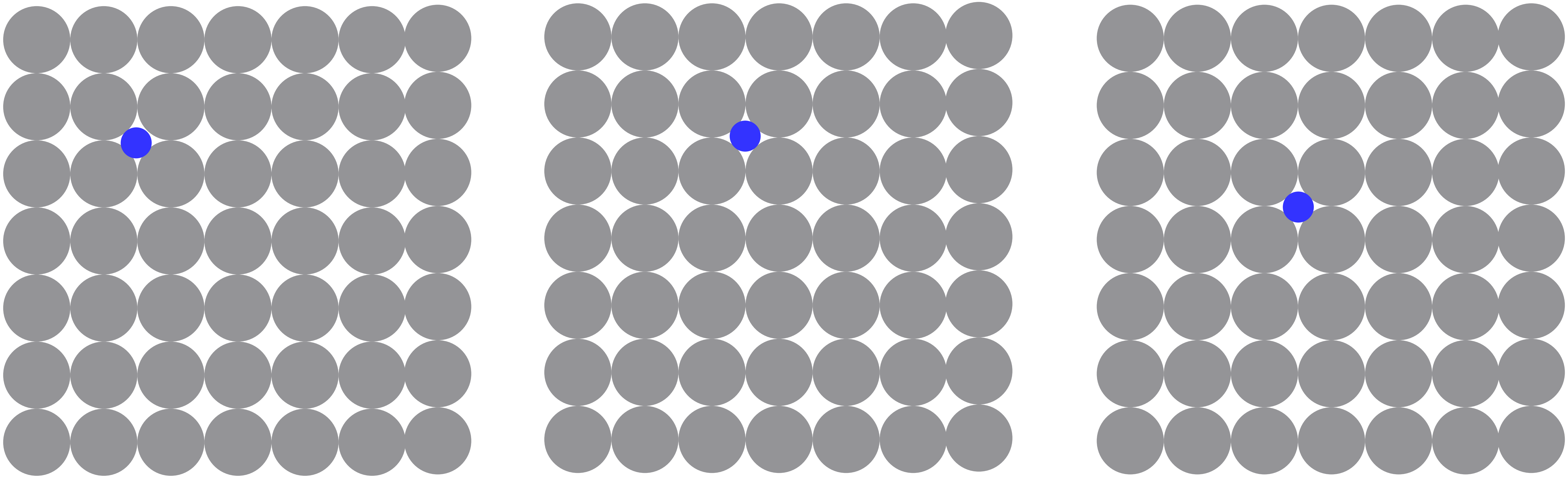
- Food packaging to preserve freshness:
  - CO_2 diffuses out from bottles
  - O_2 diffuses into the bottles

- Paints applied to metal surface to prevent corrosion:
  - O_2, H_2O, and salt diffuse through paint layer (even undamaged) to corrode metals underneath

http://www.core77.com/posts/38703/Disguising-Your-Car-with-Fake-Rust-Looks-Interesting-But-Wont-Prevent-Someone-From-Stealing-It

Mechanism #1 - Interstitial Diffusion

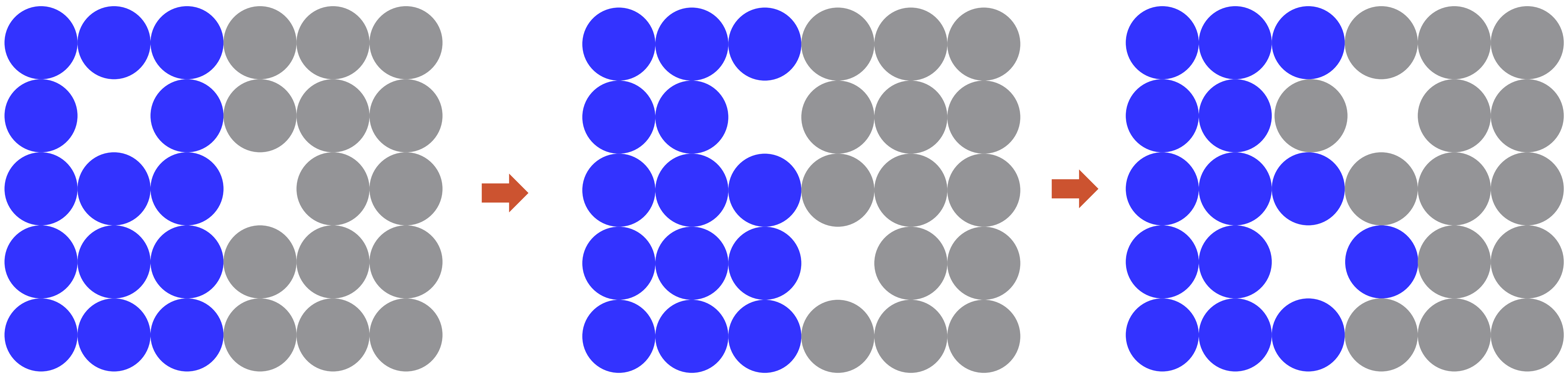
- **Interstitial diffusion:** atoms/ions/molecules **much smaller** than host can diffuse through the interstitial sites (i.e., opening) between larger host atoms/molecules.



Mechanism #2 - Substitutional Diffusion via Vacancy Exchange

For pure elements or alloys with similar sized atoms (e.g., Ni-Cu alloy)

- Diffusion occurs through atoms exchange positions with vacancies
- For diffusion of substitutional impurity atoms as well as self diffusion
- Rate of substitutional diffusion depends on
  - Vacancies concentration
  - Activation energy (energy barrier in exchanging position)



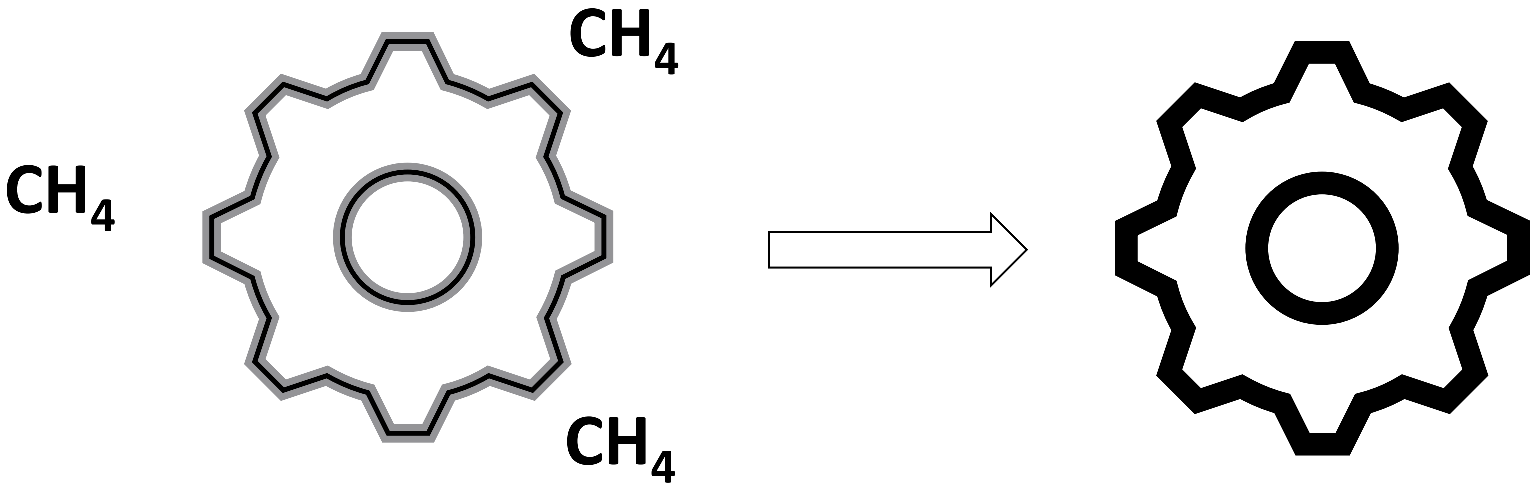
- Substitutional diffusion by vacancy exchange much **“slower”** than interstitial diffusion

Materials Processing Using Diffusion (1)

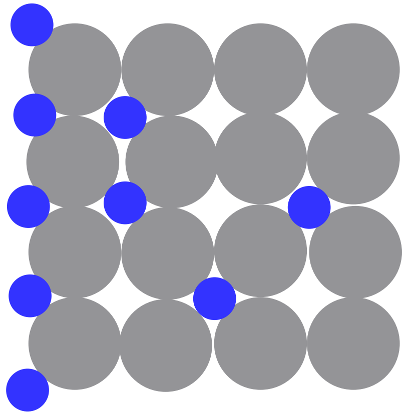
- Example – **case hardening/carburization**:
  The surface (case) of a steel gear needs to be hard (for wear resistance), while the inside needs to be tough (not brittle)

https://en.wikipedia.org/wiki/Case-hardening

- Approach: Diffuse carbon (atoms) into the surface of the low carbon steel (iron) gear via heat treatment (>~800^{o}C) in a carbon-rich atmosphere

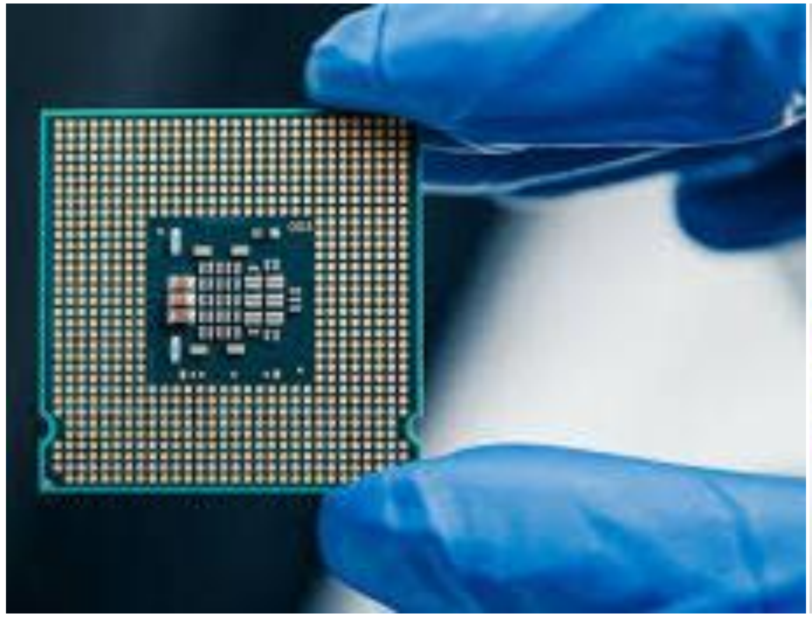


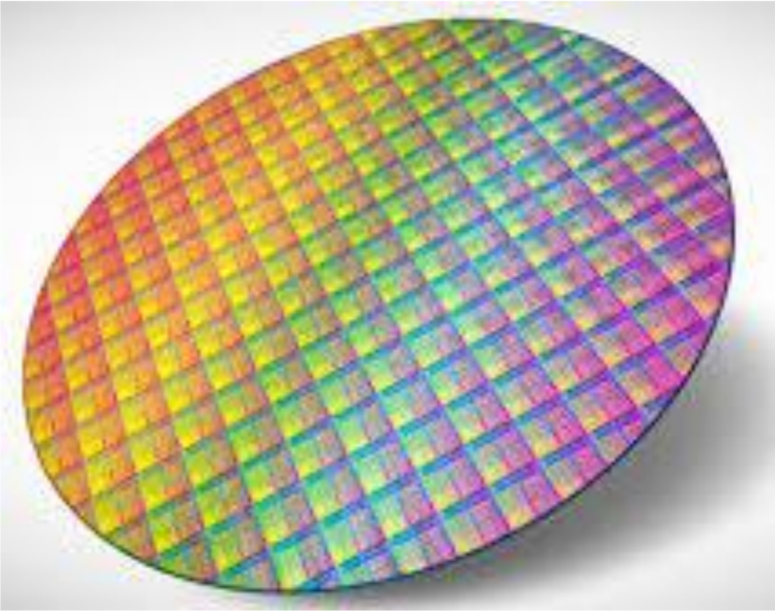
- Carbon atoms much smaller than iron (Fe) atoms:
  (r(C) = 0.07 nm; r(Fe) = 0.140 nm) - interstitial diffusion

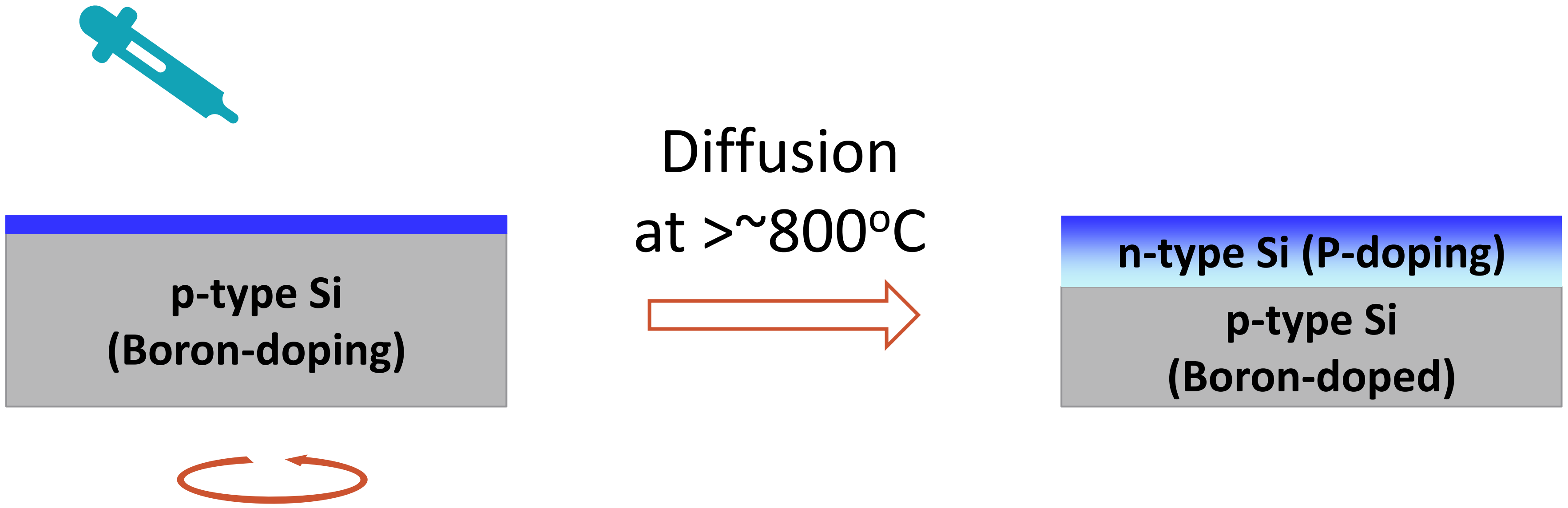


Materials Processing Using Diffusion (2)

- Forming p-n junction over p-type silicon for solar cell or silicon chip by diffusing P into Si using chemicals such as H_3PO_4, $POCl_3$ at 800°C and above







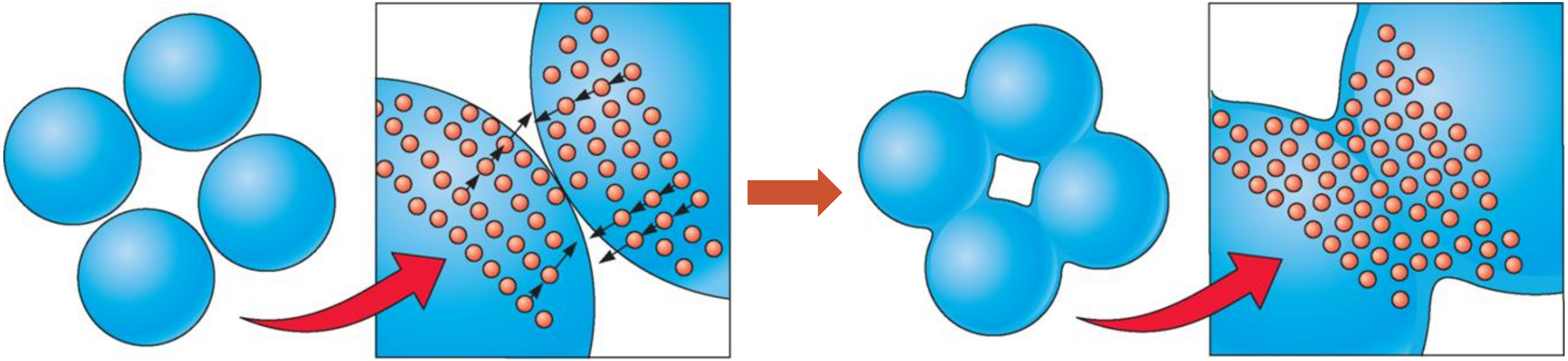
Diffusion
at >~800°C

Materials Processing Using Diffusion (3)

- Ceramics (and some metals such as tungsten) need "sintering" to bond loose powders into dense bulk materials for applications

Need firing/sintering at high temperature (e.g., >~1000^{o}C)

- During sintering, atoms diffuse so that powders get bonded and pores eliminated



Rate of Diffusion - Diffusional Flux

- **Diffusional flux** J

  Transport or flow of substance (in mass/gram or mole) per unit area per unit time

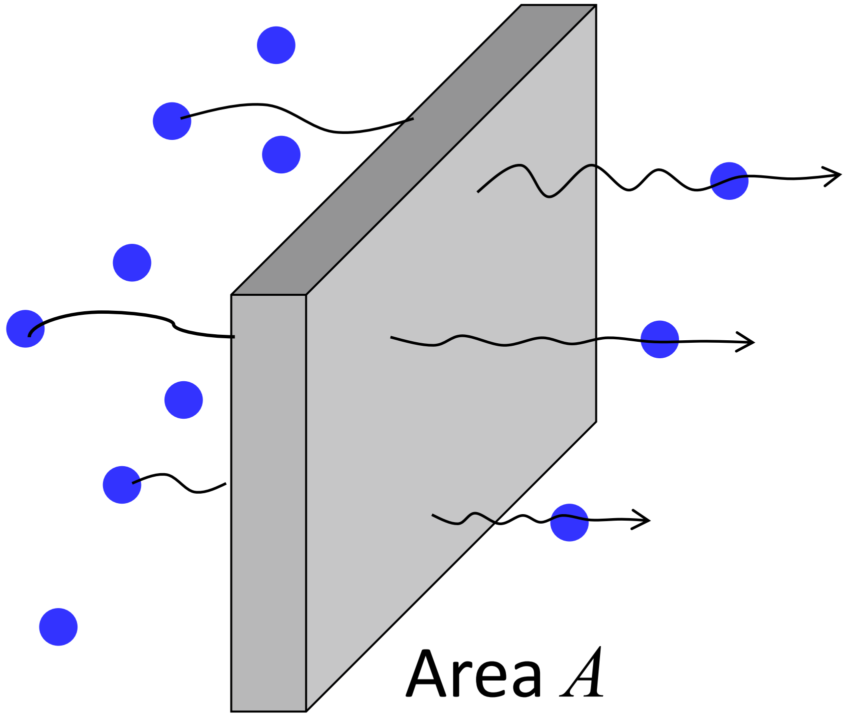
$$J = \frac{\text{moles or mass of diffusing species}}{A \cdot t}$$

Unit: $\frac{\text{mol}}{\text{cm}^2\text{s}}$ or $\frac{\text{kg}}{\text{m}^2\text{s}}$ or similar

- **Measurement of diffusional flux** J
  - Apply concentration gradient for species of interest over membrane of known surface area
  - Measure the amount of species going through the membrane

$$J = \frac{1}{A} \cdot \frac{dM}{dt}$$

If constant flux $J = J_{average} = \frac{1}{A} \cdot \frac{\Delta M}{\Delta t}$

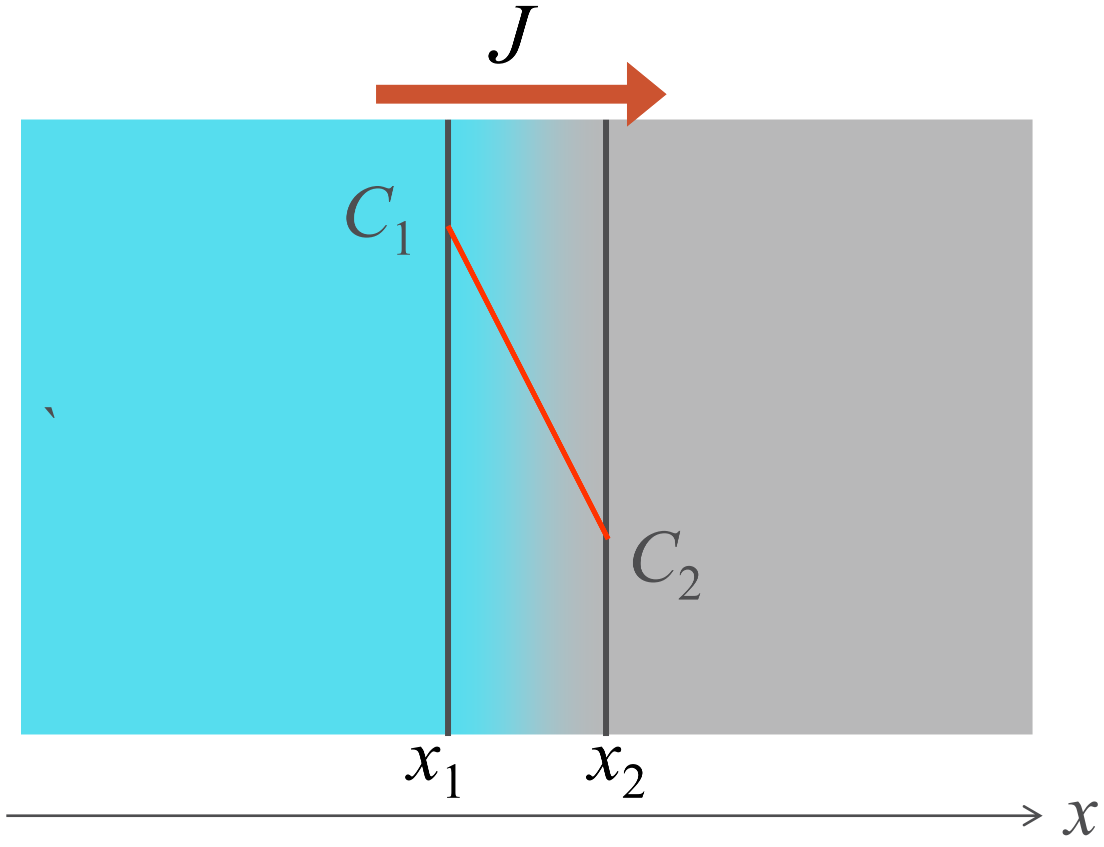


Fick's 1st Law for Diffusion

- Diffusional flux in 1D

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

C	Concentration for the diffusing species, often in unit of **mole/cm³** or similar
x	Distance, in unit of **cm** or similar
D	**Diffusion coefficient**, in unit of **cm²/sec** or similar
$\frac{dC}{dx}$	Concentration gradient along x direction



- If linear concentration profile

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

- Inter-diffusion "stops" when $\frac{dC}{dx} = 0$

  i.e., reaching uniform concentration

  Or "equilibrium"

Class Example: Chemical Flux through Rubber Glove (1)

Harmful chemical A is a common paint remover ingredient.

Rubber gloves should be worn to mitigate contact with A.

- Glove thickness is 0.5 mm
- Outside glove concentration is 0.51 g/cm^3
  Inside (touching skin) concentration is 0.01 g/cm3
- Chemical A has diffusion coefficient of 100x10^{-8} cm^2/s through glove material.

1) Calculate the diffusive flux of chemical A through the glove, assuming linear concentration profile of A through the glove thickness
2) Assuming glove total surface area of 300 cm^2, estimate the total amount of chemical A that is passing through a glove in 1 min use and 1 h use, respectively.

Flux from Fick's 1st law $J = -D\frac{dC}{dx}$

$\Delta x = 0.5\ mm$

$C_{outside} = 0.51\ g/cm^3$

$C_{inside} = 0.01\ g/cm^3$

$D = 100 \times 10^{-8}\ cm^2/s$

Linear concentration profile $|J| \approx D\frac{\Delta C}{\Delta x} = D\frac{C_{outside} - C_{inside}}{\Delta x}$

https://www.onlinesafetytrainer.com/how-to-select-the-appropriate-chemical-resistant-glove/

Class Example: Chemical Flux through Rubber Glove (2)

1) A diffusive flux through glove

$$|J| \approx D\frac{\Delta C}{\Delta x} = D\frac{C_{outside} - C_{inside}}{\Delta x} = 100 \times 10^{-8}\,\frac{cm^2}{s} \times \frac{0.51\,\frac{g}{cm^3} - 0.01\,\frac{g}{cm^3}}{0.5\ mm}$$

$$= 100 \times 10^{-8}\,\frac{cm^2}{s} \times \frac{0.5\,\frac{g}{cm^3}}{0.05\ cm} = 1 \times 10^{-5}\,\frac{g}{cm^2 \cdot s}$$

2) Flux definition: $\boxed{J = \frac{\text{moles or mass of diffusing species}}{A \cdot t}} = \frac{1}{A} \cdot \frac{\Delta M}{\Delta t}$ assuming constant flux J

Quantity of A diffusing through 300 cm^2 glove in 1 min

$$\Delta M = |J| \cdot A \cdot \Delta t = 1 \times 10^{-5}\,\frac{g}{cm^2 \cdot s} \times 300cm^2 \times 60s = 0.18\ g$$

Quantity of A diffusing through 300 cm^2 glove in 1 h

$$\Delta M = |J| \cdot A \cdot \Delta t = 1 \times 10^{-5}\,\frac{g}{cm^2 \cdot s} \times 300cm^2 \times 3600s = 10.8\ g$$

$\Delta x = 0.5\ mm$

$C_{outside} = 0.51\ g/cm^3$

$C_{inside} = 0.01\ g/cm^3$

$D = 100 \times 10^{-8}\ cm^2/s$

To reduce harmful chemical exposure: reduce (outside) concentration & use time

Temperature Effect on Diffusion (1)

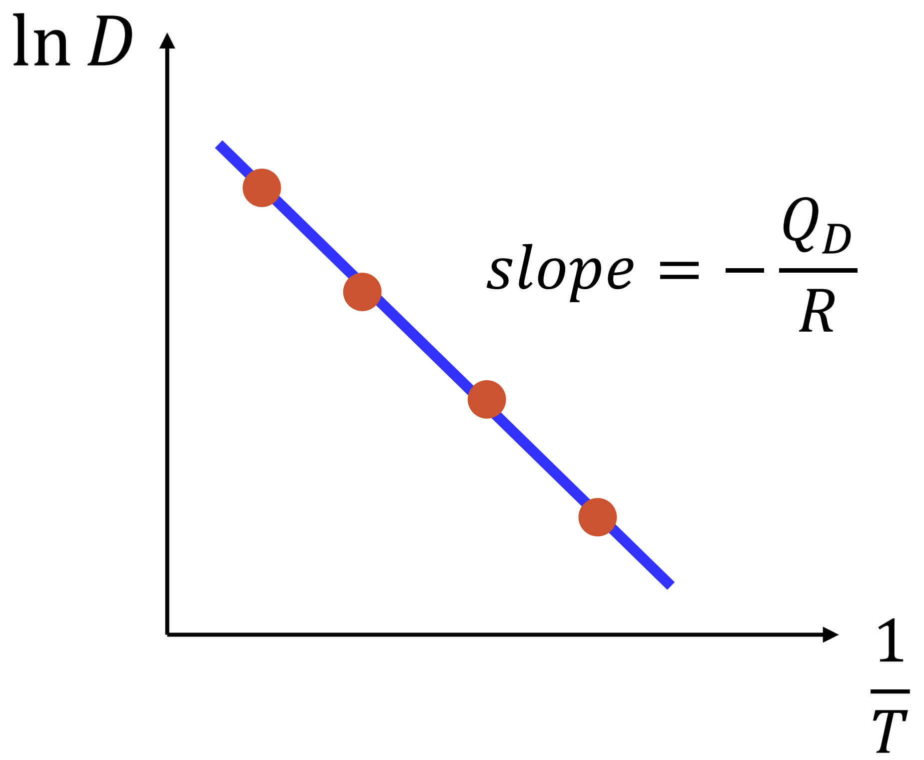
- Diffusion coefficient increases “exponentially” with increasing temperature T

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

D_0	Pre-exponential term, unit of **cm²/s** or similar
T	Temperature, in unit of K
R	Ideal gas constant 8.314 J/(mol • K)
Q_D	Diffusion activation energy, unit of J/mol

Re-arrange

$$\ln D = \ln D_0 - \left(\frac{Q_D}{R}\right) \cdot \frac{1}{T}$$



Diffusion Coefficient at Different Temperature Example (1)

The diffusion coefficient for Cu in Si is 7.8 x 10^{-11} m^2/s at 300°C.
If the diffusion activation energy is 41.5 kJ/mol,
what is Cu diffusion coefficient in Si at 400°C?

$$D_{300C} = 7.8 \times 11\ m^2/s$$

$$Q_D = 41.5\ kJ/mol$$

Dependence of diffusion coefficient on temperature:

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

Known $D_{300C} = D_0 \exp\left(-\frac{Q_D}{RT_{300C}}\right)$

Want $D_{400C} = D_0 \exp\left(-\frac{Q_D}{RT_{400C}}\right)$

Take ratio: $\frac{D_{400C}}{D_{300C}} = \frac{\exp\left(-\frac{Q_D}{RT_{400C}}\right)}{\exp\left(-\frac{Q_D}{RT_{300C}}\right)}$ ➡ $D_{400C} = D_{300C} \exp\left(\frac{Q_D}{RT_{300C}} - \frac{Q_D}{RT_{400C}}\right)$

Diffusion Coefficient at Different Temperature Example (2)

From previous: $$D_{400C} = D_{300C} \exp\left(\frac{Q_D}{RT_{300C}} - \frac{Q_D}{RT_{400C}}\right) = D_{300C} \exp\left[\frac{Q_D}{R} \cdot \left(\frac{1}{T_{300C}} - \frac{1}{T_{400C}}\right)\right]$$

$$D_{400C} = 7.8 \times 10^{-11} \frac{m^2}{s} \times \exp\left[\frac{41500 \frac{J}{mol}}{8.314 \frac{J}{mol \cdot K}} \times \left(\frac{1}{300 + 273K} - \frac{1}{400 + 273K}\right)\right]$$

$$= 2.85 \times 10^{-10} \frac{m^2}{s}$$

$D_{300C} = 7.8 \times 11\ m^2/s$

$Q_D = 41.5\ kJ/mol$

Alternatively, $D_{300C} = D_0 \exp\left(-\frac{Q_D}{RT_{300C}}\right)$

$$D_0 = D_{300C} \exp\left(\frac{Q_D}{RT_{300C}}\right) = 7.8 \times 10^{-11} \frac{m^2}{s} \times \exp\left[\frac{41500 \frac{J}{mol}}{8.314 \frac{J}{mol \cdot K} \times (300 + 273)K}\right] = 4.74 \times 10^{-7} \frac{m^2}{s}$$

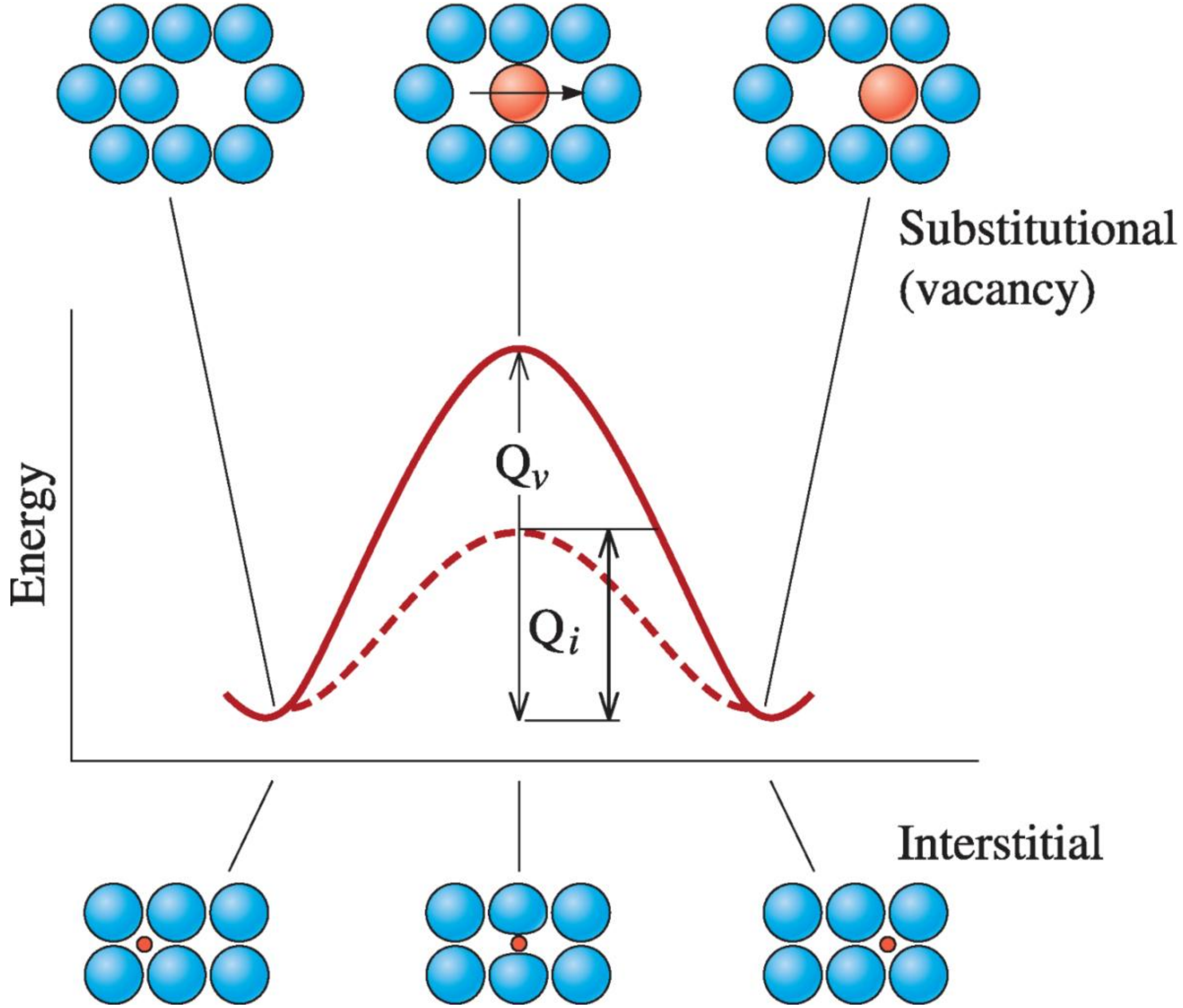
$$D_{400C} = D_0 \exp\left(-\frac{Q_D}{RT_{400C}}\right) = 4.74 \times 10^{-7} \frac{m^2}{s} \times \exp\left[-\frac{41500 \frac{J}{mol}}{8.314 \frac{J}{mol \cdot K} \times (400 + 273)K}\right] = 2.85 \times 10^{-10} \frac{m^2}{s}$$

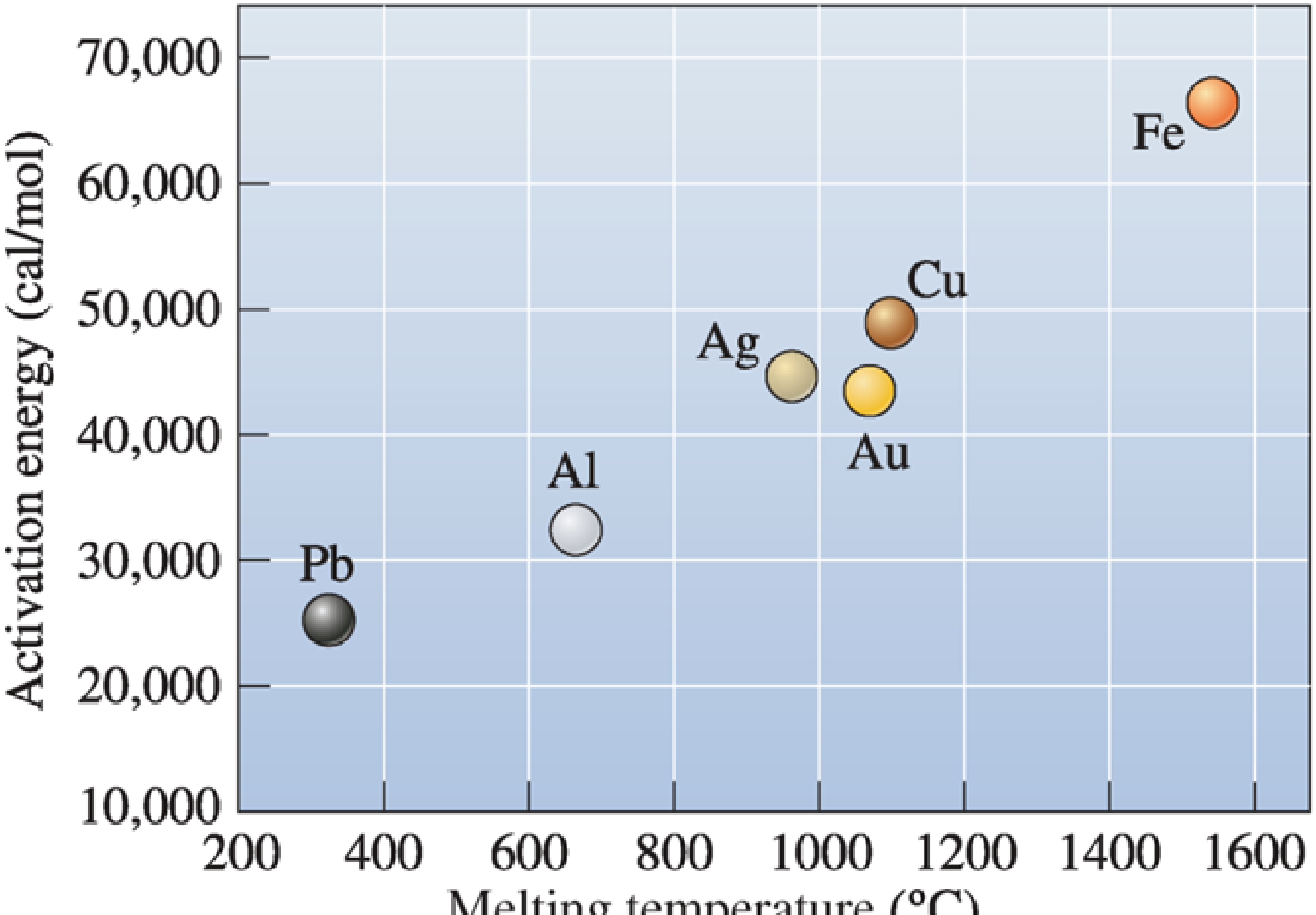
Diffusion Activation Energy Q_D

- Diffusion coefficient increases “exponentially” w/ temperature

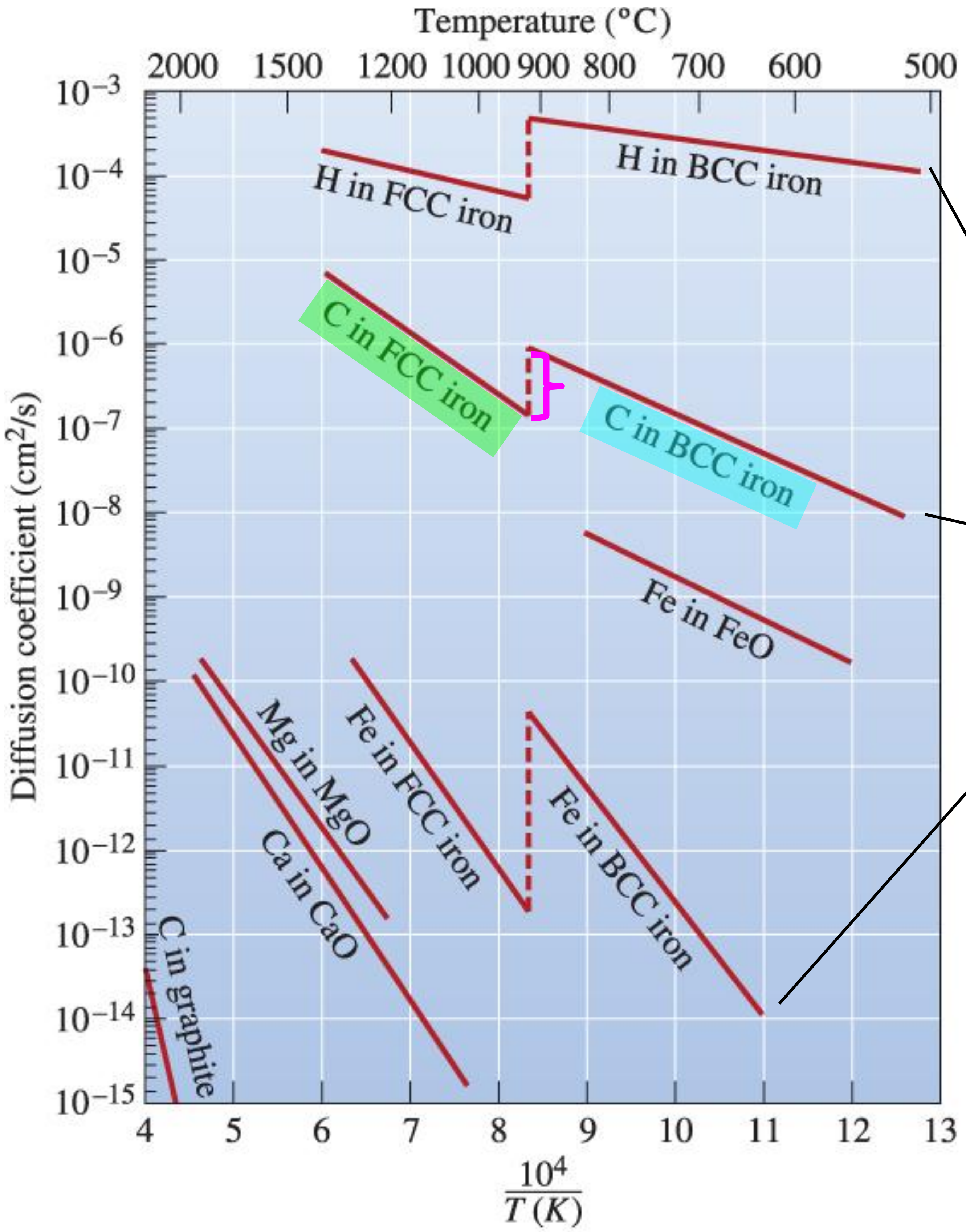
$$D = D_0 \exp\left(-\frac{Q_D}{RT}\right)$$

- Q_D represents energy barrier that atoms, ions, or molecules have to go over to move to an available, neighboring site and it depends strongly on bonding in host material





Other Factors on Diffusion Coefficient D



- Smaller diffusing species, lower Q_D (and higher D, in a range)
  - **Example:**

    H in BCC Fe → Low Q_D
    C in BCC Fe → Medium Q_D
    Fe in BCC Fe → High Q_D

- Lower host (atoms) packing density, lower Q_D (and higher D, in a range)
  - Example:

    C in BCC Fe (68% packing density) → Low Q_D
    C in FCC Fe (74% packing density) → High Q_D

Fick's 2nd Law for Diffusion

Due to diffusion, concentration of diffusing species is also a function of time, i.e.,

$$C = C(x, t)$$

Fick's 2nd Law

Local rate of concentration change with time, for 1D diffusion would be:

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

If D is a constant (i.e., does not change with concentration), can **simplify** as:

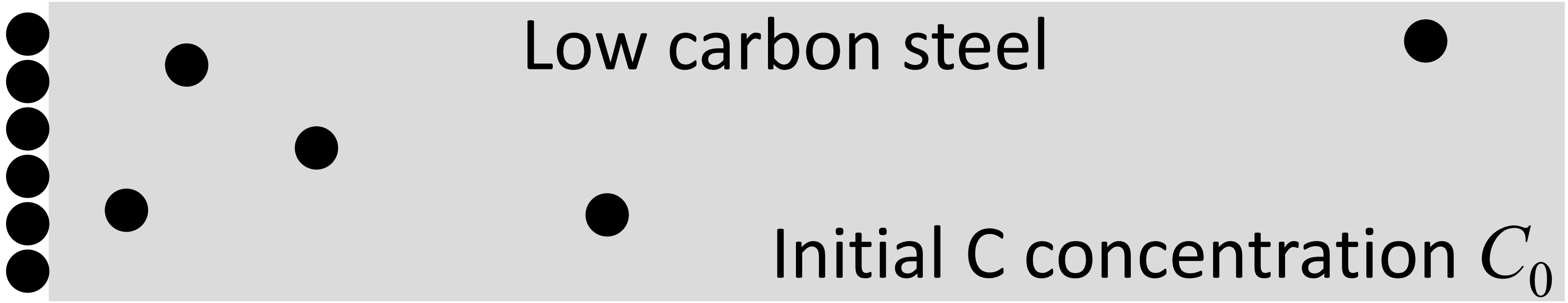
$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2}$$

Fick's 2nd law equation might have analytical solution under some special conditions

Case Hardening (Carburization) Example (1)

- Diffuse carbon into surface of low carbon steel to make surface harder:

Fixed surface carbon concentration C_S



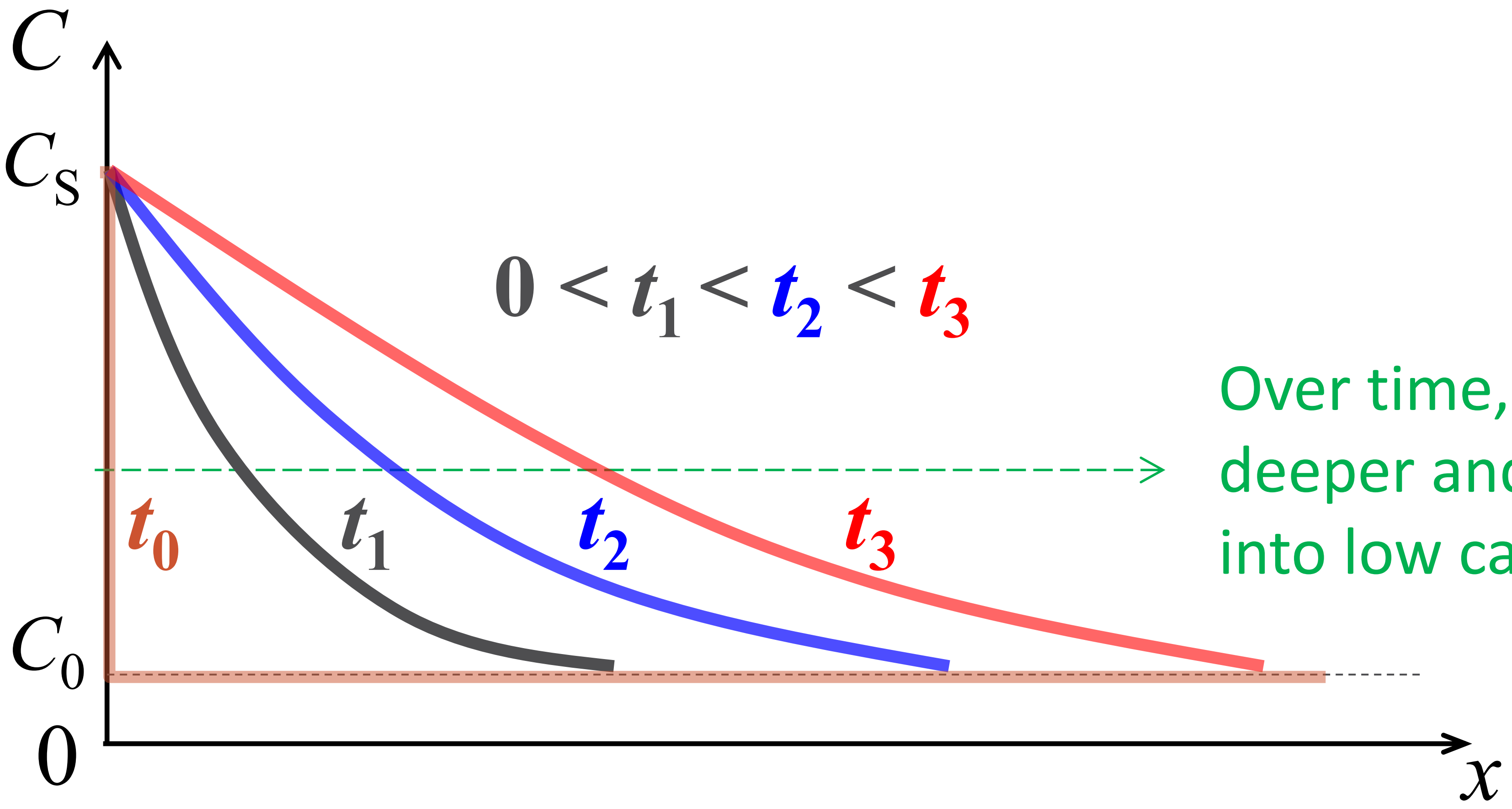
- Local carbon concentration changes with location and time

Assume D constant

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} \Rightarrow C(x,t)?$$

<u>Boundary conditions</u> (BC)

- $t = 0$, $C = C_0$ for $0 \le x \le \infty$
- $t > 0$, $C = C_S$ for $x = 0$ (constant surface conc.)
- $t > 0$, $C = C_0$ for $x = \infty$ (deep inside not impacted)



Over time, C diffuses deeper and deeper into low carbon steel

Case Hardening (Carburization) Example (2)

Analytical solution to Fick's 2nd law equation, using the BCs:

$$\frac{C(x,t) - C_0}{C_S - C_0} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Or $$C(x,t) = C_S - (C_S - C_0)\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Error function is defined below (see right for some values) :

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

Can be used to determine:

- $C(x,t)$ - concentration profile at any time *t*
- D, t, or x , if other parameters are all known

z	erf(z)	z	erf(z)
0	0.0000	0.85	0.7707
0.05	0.0564	0.90	0.7969
0.10	0.1125	0.95	0.8209
0.15	0.1680	1.00	0.8427
0.20	0.2227	1.10	0.8802
0.25	0.2763	1.20	0.9103
0.30	0.3286	1.30	0.9340
0.35	0.3794	1.40	0.9523
0.40	0.4284	1.50	0.9661
0.45	0.4755	1.60	0.9763
0.50	0.5205	1.70	0.9838
0.55	0.5633	1.80	0.9891
0.60	0.6039	1.90	0.9928
0.65	0.6420	2.00	0.9953
0.70	0.6778	2.20	0.9981
0.75	0.7112	2.40	0.9993
0.80	0.7421	2.60	0.9998

Carburization Example for Fick's 2nd Law (1)

- A 0.1% carbon steel is treated for case hardening via carburization process
- Surface carbon concentration is fixed at 1.1%.
- The steel needs to have 0.5% carbon at a depth of 0.25 cm below the surface

How much **time** is needed if the carburization process is carried out at 1200 K (923°C)? What about at 1500K (1223°C)?

Known: C diffusion pre-exponential term 0.23 cm^2/s; activation energy = 137.5 kJ/mol

Analytical solution for diffusion in case hardening: $C(x,t) = C_S - (C_S - C_0)\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$

Known: $C_0 = 0.1\%$ $C_S = 1.1\%$ $C(x,t) = 0.5\%$ $x = 0.25cm$

$t = ??$

Temperature effect on diffusion coefficient? $D = D_0 \exp\left(-\frac{Q_D}{RT}\right)$ $D_0 = 0.23\ \frac{cm^2}{s}$ $Q_D = 137.5\ \frac{kJ}{mol}$

Carburization Example for Fick's 2nd Law (2)

$$C(x,t) = C_S - (C_S - C_0)\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Known: $C_0 = 0.1\%$ $C_S = 1.1\%$ $C(x,t) = 0.5\%$ $x = 0.25cm$

Plug numbers in $0.5\% = 1.1\% - (1.1\% - 0.1\%) \times \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$

z	erf(z)
0.55	0.5633
0.60	0.6039
0.65	0.6420

$$\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{1.1\% - 0.5\%}{1\%} = 0.6$$

From error function table, interpolate: $\frac{x}{2\sqrt{Dt}} \approx 0.595$ → $\frac{x^2}{4Dt} \approx 0.595^2$

$$t = \frac{x^2}{4D \times 0.595^2} = \frac{(0.25\ cm)^2}{4 \times 0.595^2} \cdot \frac{1}{D} = 0.0441cm^2 \cdot \frac{1}{D_0}\exp\left(\frac{Q_D}{RT}\right)$$

$$\left\{\begin{aligned} D_0 &= 0.23\ \frac{cm^2}{s} \\ Q_D &= 137.5\ \frac{kJ}{mol} \\ R &= 8.314\ \frac{J}{mol \cdot K} \end{aligned}\right.$$

$T = 1200\ \mathrm{K}$ $t = 185.6 \times 10^3\ \mathrm{s} = \mathbf{51.6\ h}$

$T = 1500\ \mathrm{K}$ $t = 11.76 \times 10^3\ \mathrm{s} = \mathbf{3.3\ h}$

Diffusion (Characteristic) Length

The depth (length) within which significant (concentration) change has happened due to diffusion

$$x \approx \sqrt{Dt}$$

Carburization example:

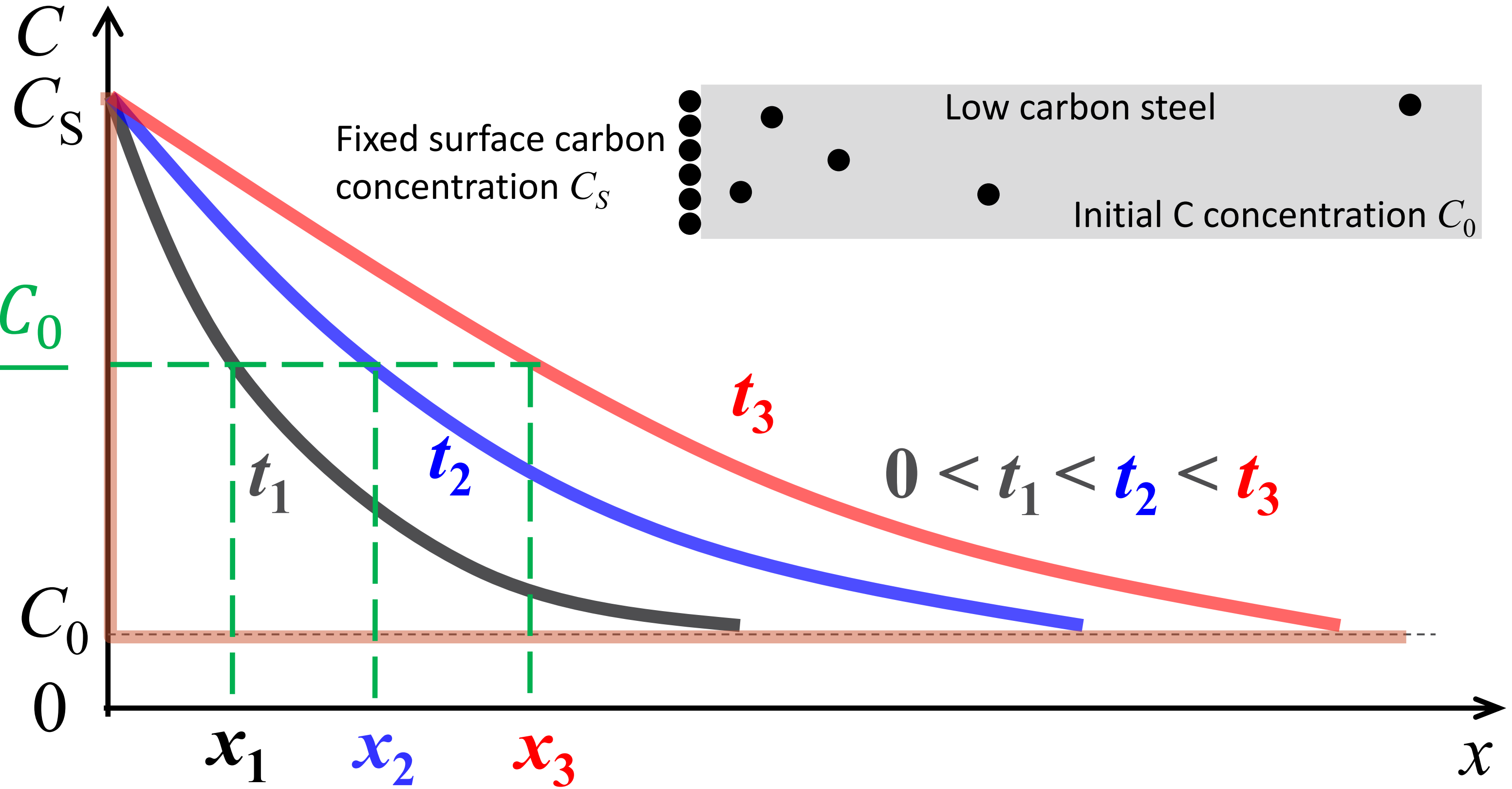
$$C(x,t) = C_S - (C_S - C_0)\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

When $C(x,t)$ increases from C_0 to $\frac{C_S + C_0}{2}$

$$\frac{C_S + C_0}{2} = C_S - (C_S - C_0)\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$(C_S - C_0)\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{C_S - C_0}{2}$$

$$\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{1}{2} \Rightarrow \frac{x}{2\sqrt{Dt}} \approx \frac{1}{2} \Rightarrow x \approx \sqrt{Dt}$$



At t_1, diffusion length: $x_1 \approx \sqrt{Dt_1}$

To double diffusion length, from x_1 to $2x_1$:

$$x_2 = \sqrt{Dt_2} = 2x_1 = 2\sqrt{Dt_1} \Rightarrow t_2 = 2^2 t_1$$

To triple diffusion length (to $3x_1$), $t_3 = ?$

Diffusion Length Class Example

Diffusion coefficient for P and Cu in Si at 1000°C is 1×10^{-14} cm^2/s and 5.3×10^{-6} cm^2/s, respectively. If Cu and P are deposited on surface of Si, please estimate the depth within Si that is significantly impacted by P and Cu diffusion after 30 min at 1000°C.

For P diffusion in Si, diffusion length (or depth significantly impacted) at 1000°C for 30 min:

$$x_{\mathrm{P}} \approx \sqrt{D_P t} = \sqrt{10^{-14}\,\frac{cm^2}{s} \times 1800\ \mathrm{s}} = 4.2 \times 10^{-6} cm = \mathbf{42\ nm}$$

For Cu diffusion in Si, diffusion length (or depth impacted by diffusion) at 1000°C for 30 min:

$$x_{\mathrm{Cu}} \approx \sqrt{D_{Cu} t} = \sqrt{5.3 \times 10^{-6}\,\frac{cm^2}{s} \times 1800\ \mathrm{s}} = 0.098\ cm = \mathbf{0.98\ mm}$$

Implications:

- Under the same condition (temperature, time), Cu would diffuse (penetrate) much deeper than P into Si!
- Since Cu is detrimental to Si devices, a "**diffusion barrier**" (e.g., Ru or TaN) for copper has to be applied in the semiconductor industry when using Cu as metal conductor for Si micro-chips

END

Homework 5.0

Carefully review chapter 5 lecture slides and, if time allows, read textbook sections (Askeland chapter 5) and give an honor statement confirming the reading

Homework 5.1

- Explain briefly, in your own words, the difference between self-diffusion and inter-diffusion
- Compare briefly, in your own words, interstitial diffusion mechanism versus substitutional diffusion via vacancy exchange mechanism

Homework 5.2

Calculate the mass of H_2 gas that passes in five hour through a 2-mm thick Pd metal membrane with area of 0.25 m^2 at 500°C.

Known H_2 diffusion coefficient through Pd is 1.0×10^{-4} cm^2/s, while concentrations at two sides of the membrane are 3.0 and 0.5 kg of H_2 per cubic meter of Pd metal

Assume steady-state condition, i.e., constant H_2 diffusion flux and constant H_2 concentration gradient

Homework 5.3

The diffusion coefficients for aluminum in copper is 5.81×10^{-12} cm^2/s at 600°C and 4.05×10^{-10} cm^2/s at 800°C. Please:

1) Determine the values of pre-exponential term D_0 and diffusion activation energy Q_d.
2) What is the diffusion coefficient at 700°C?

Homework 5.5

An FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere that gives a surface carbon concentration constant at 1.2 wt%. If after 50 h the concentration of carbon is 0.4 wt% at a position 0.5 cm below the surface, please determine the diffusion coefficient.

Homework 5.4

The diffusion coefficient for Al in Cu at 400 and 500 °C are 6.69×10^{-15} and 3.05×10^{-13} cm^2/s, respectively. Determine the approximate time at 400 °C that will produce the same diffusion result (i.e., diffusion length) as a 10 hour heat treatment at 500 °C. Note that diffusion length $x \approx \sqrt{Dt}$