

# Chapter 5: Diffusion (2)

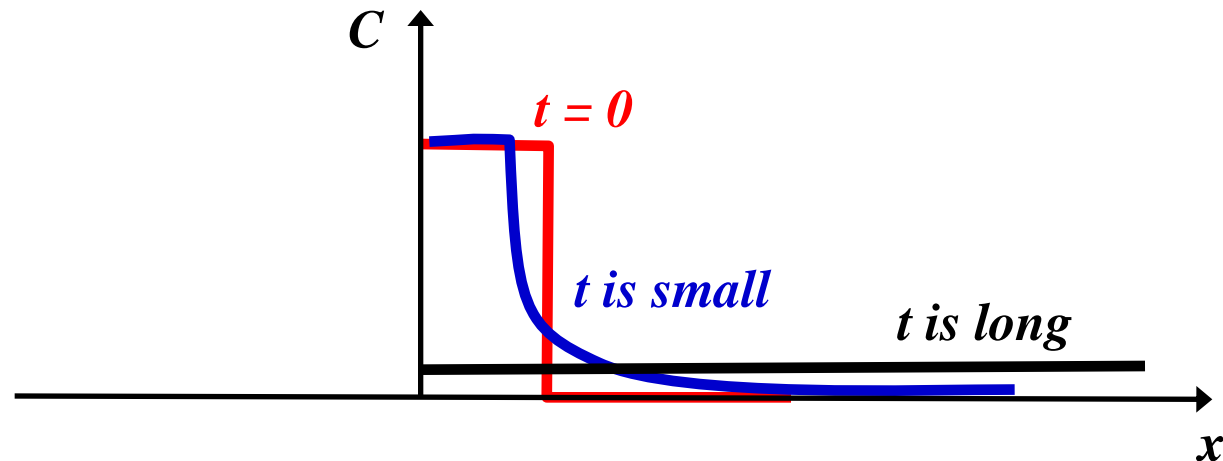
## ISSUES TO ADDRESS...

- Non-steady state diffusion and Fick's 2<sup>nd</sup> Law
- How does diffusion depend on structure?



# Class Exercise (1)

- Put a sugar cube inside a cup of pure water, roughly draw the sugar concentration profile inside the water for i) time is zero (i.e., right after the sugar cube was placed in water), ii) after a short time (e.g., 30 sec) and iii) after very long time



## Class Exercise (2)

- Given Fick's 1<sup>st</sup> Law in 1D,  $J = -D \frac{dC}{dx}$ 
  - 1) Explain the physical meaning for each of the terms in the equation and their unit
  - 2) if both flux J and diffusion coefficient D are constants, prove the concentration change linearly with position

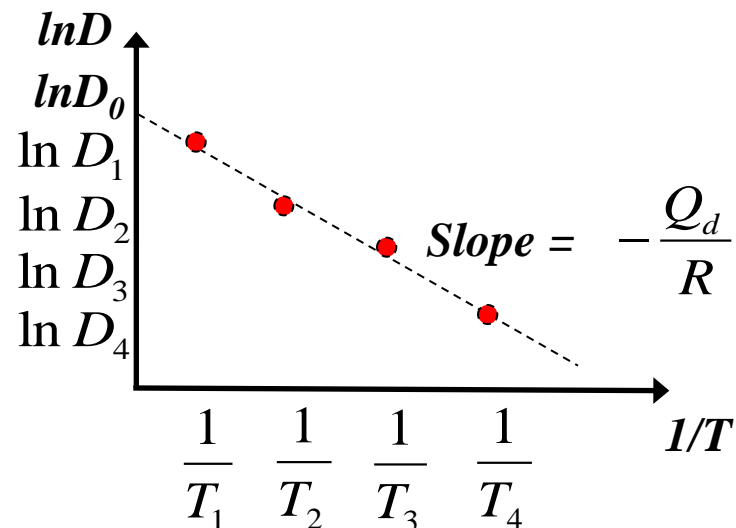


# Class Exercise (3)

- If diffusion coefficient at different temperatures (i.e.,  $D_1$  at  $T_1$ ,  $D_2$  at  $T_2$ ,  $D_3$  at  $T_3$ ,  $D_4$  at  $T_4$ ) are measured, describe how to mathematically determine diffusion activation energy  $Q_d$

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

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



# Non-Steady State Diffusion

- General case:  
The concentration of diffusing species is a function of position, time, and, maybe, concentration  $C = C(x, t, c)$
- Fick's Second Law

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

- If  $D$  is a constant (i.e., does not change with concentration)

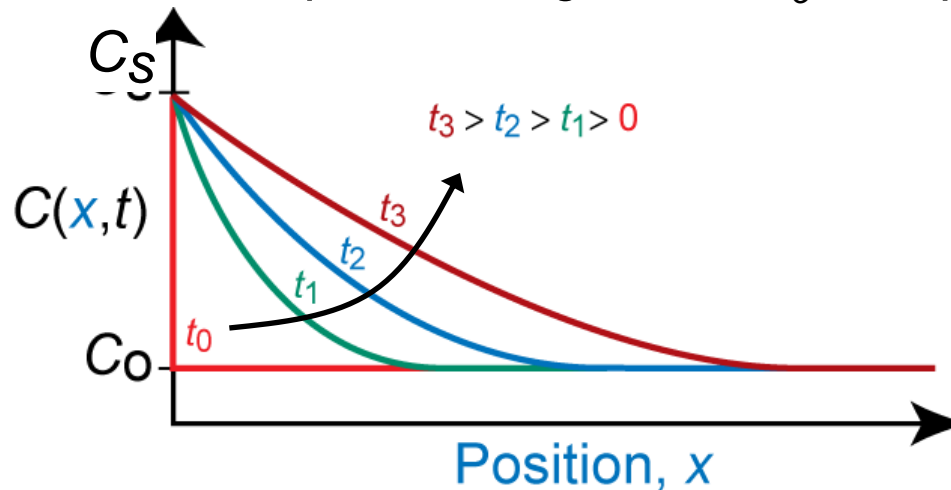
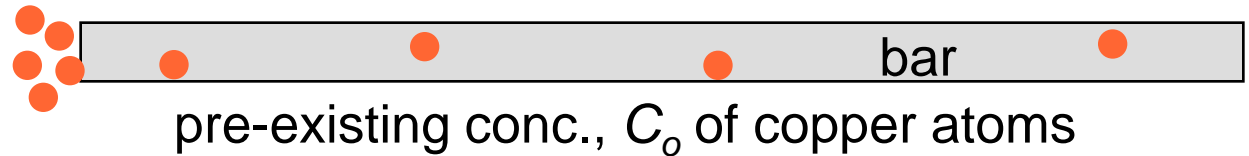
$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$



# Special Example for Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.

Surface conc.,  
 $C_S$  of Cu atoms



Adapted from  
Fig. 5.5,  
Callister &  
Rethwisch 8e.

Fick's 2<sup>nd</sup> law  $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \Rightarrow C(x, t)?$

Boundary conditions

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

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

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



# Solution:

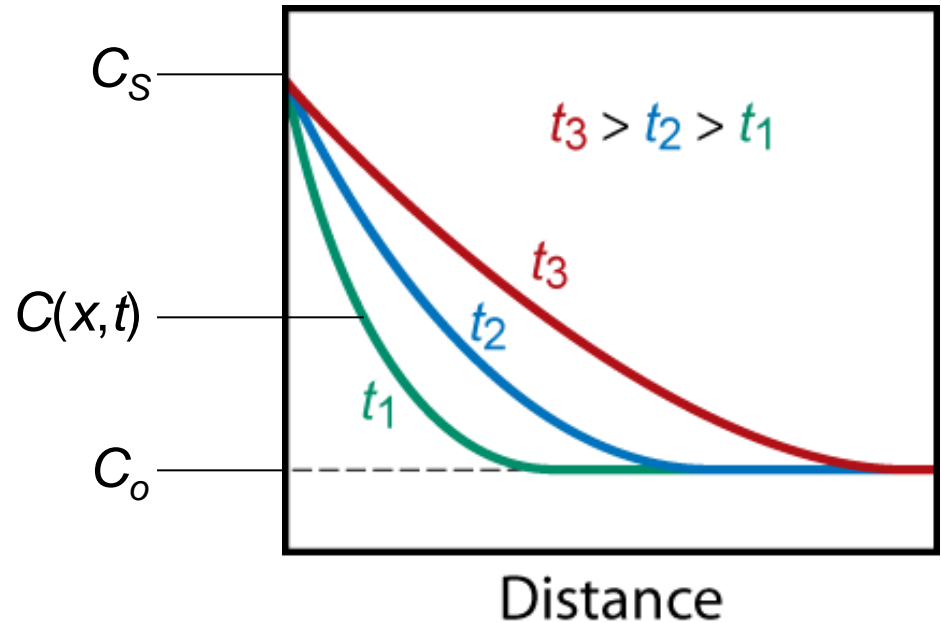
$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$C(x,t)$  = Conc. at point  $x$  at time  $t$

$\operatorname{erf}(z)$  = error function

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

$\operatorname{erf}(z)$  values are given in Table 5.1



Adapted from Fig. 5.5,  
*Callister & Rethwisch 8e.*



# Example of a Special Case for Non-steady State Diffusion

- Problem: 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 1.0 wt%. If after 49.5 h the concentration of carbon is 0.35 wt% at a position 4.0 mm below the surface, determine the diffusion coefficient. Knowing concentration at time  $t$  and position  $x$  satisfy the following relationship:

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

$$t = 49.5 \text{ h}$$

$$x = 4 \times 10^{-3} \text{ m}$$

$$C_x = 0.35 \text{ wt}\%$$

$$C_s = 1.0 \text{ wt}\%$$

$$C_o = 0.20 \text{ wt}\%$$





**Solution (cont.):** 
$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

–  $t = 49.5 \text{ h}$

$x = 4 \times 10^{-3} \text{ m}$

–  $C_x = 0.35 \text{ wt\%}$

$C_s = 1.0 \text{ wt\%}$

–  $C_o = 0.20 \text{ wt\%}$

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

$\therefore \operatorname{erf}(z) = 0.8125$



## Solution (cont.):

We must now determine the value of  $z$  for which the error function is 0.8125. If as in Table 5.1 in textbook, tabulated data are given, an interpolation can be used to obtain the approximate value

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

$$\frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}$$

$$z = 0.93$$

Now solve for  $D$

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

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



# Diffusion Length

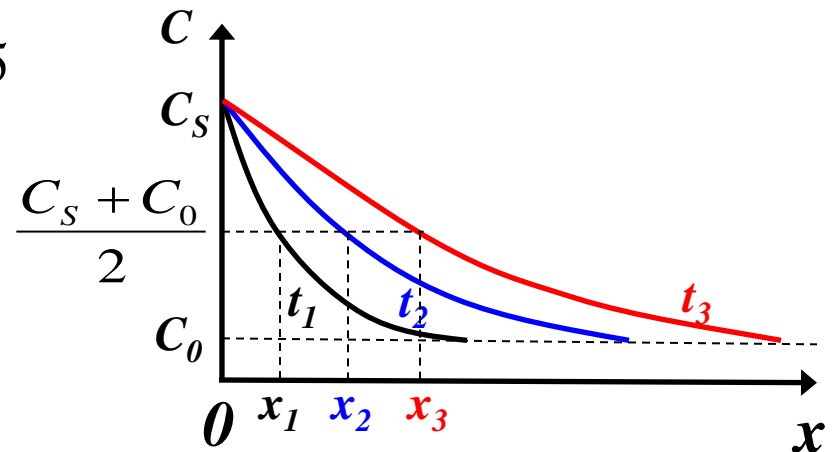
$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

• **When**  $\frac{C - C_o}{C_s - C_o} = 0.5$        $C = \frac{C_o + C_s}{2}$

$$\frac{C - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.5$$

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.5$$

$$z = \frac{x}{2\sqrt{Dt}} \approx 0.5$$



• **Diffusion (characteristic) length**

The depth (length) within which significant diffusion has happened

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



# Class Exercise

- **Knowing diffusion length**

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

Diffusion coefficient for P and Cu in Si at 1000C is  $1 \times 10^{-14} \text{ cm}^2/\text{sec}$  and  $5.3 \times 10^{-6} \text{ cm}^2/\text{sec}$ , respectively. If putting Cu and P on surface of Si, please estimate the depth within silicon that is impacted by P and Cu diffusion after 30 min at 1000C, respectively

$$x_P \approx \sqrt{Dt} = \sqrt{10^{-14} \text{ cm}^2 / \text{sec} \times 1800 \text{ sec}}$$
$$= 4.2 \times 10^{-6} \text{ cm} = 42 \text{ nm}$$

$$x_{Cu} \approx \sqrt{Dt} = \sqrt{5.3 \times 10^{-6} \text{ cm}^2 / \text{sec} \times 1800 \text{ sec}}$$
$$= 0.09 \text{ cm} = 900 \mu\text{m}$$

- *At the same temperature for same time, Cu would diffuse (penetrate) much deeper than P into Si!*
- *As Cu is detrimental to Si devices, people have to apply a “diffusion barrier” (e.g., Ru or TaN) in the semiconductor industry when using Cu as metal conductor for Si micro-chips*



## Example Problem (2)

- Problem: The diffusion coefficient for copper in Al at 500 and 600 °C are  $4.8 \times 10^{-14}$  and  $5.3 \times 10^{-13}$  m<sup>2</sup>/s, respectively. Determine the approximate time at 500 °C that will produce the same diffusion result (i.e., diffusion length) as a 10 hour heat treatment at 600 °C. Note that diffusion length

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

- Same diffusion result, therefore, same diffusion length, i.e.,

$$x_1 \approx \sqrt{D_1 t_1} = \sqrt{D_2 t_2} \approx x_2$$

In this case,

$$D_1 \text{ (600°C)} = 5.3 \times 10^{-13} \text{ m}^2/\text{s},$$

$$D_2 \text{ (500°C)} = 4.8 \times 10^{-14} \text{ m}^2/\text{s}$$

$$t_1 \text{ (600°C)} = 10 \text{ h}$$

$$t_2 \text{ (500°C)} = \frac{D_1}{D_2} t_1 = 110.4 \text{ h}$$

*It would need a much longer time at lower temperature to produce the same (diffusion) result as that obtained at a higher temperature*



# Structure Effects on Diffusion

Diffusion **FASTER** for...

- More open crystal structures
- Materials w/secondary bonding
- Smaller diffusing atoms
- Lower density materials

Diffusion **SLOWER** for...

- Close-packed structures
- Materials with all covalent bonding
- Larger diffusing atoms
- Higher density materials



# Homework

- **Read chapter 5 of Callister 8ed and give an honor statement confirming you finished the required reading**
- **Callister 8ed, 5.1, 5.3(a), 5.6, 5.11, 5.16, 5.22**



- **Calister 8ed, 5.1**

**5.1 *Briefly explain the difference between self-diffusion and interdiffusion.***

- **Calister 8ed, 5.3(a)**

**5.3 (a) *Compare interstitial and vacancy atomic mechanisms for diffusion.***





## Calister 8ed, 5.6

***The purification of hydrogen gas by diffusion through a palladium sheet was discussed in Section 5.3. Compute the number of kilograms of hydrogen that pass per hour through a 5-mm-thick sheet of palladium having an area of 0.20 m<sup>2</sup> at 500°C. Assume a diffusion coefficient of  $1.0 \times 10^{-8}$  m<sup>2</sup>/s, that the concentrations at the high- and low-pressure sides of the plate are 2.4 and 0.6 kg of hydrogen per cubic meter of palladium, and that steady-state conditions have been attained.***



- **Calister 8ed, 5.11**

**5.11 Determine the carburizing time necessary to achieve a carbon concentration of 0.45 wt% at a position 2 mm into an iron–carbon alloy that initially contains 0.20 wt% C. The surface concentration is to be maintained at 1.30 wt% C, and the treatment is to be conducted at 1000°C. Use the diffusion data for  $\gamma$ -Fe in Table 5.2**



- Calister 8ed, 5.16

**5.16 Cite the values of the diffusion coefficients for the interdiffusion of carbon in both  $\alpha$ -iron (BCC) and  $\gamma$ -iron (FCC) at  $900^\circ\text{C}$  (from Table 5.2). Which is larger? Explain why this is the case.**



- Calister 8ed, 5.22

**5.22** *The diffusion coefficients for silver in copper are given at two temperatures:*

*(a) Determine the values of  $D_0$  and  $Q_d$ .*

*(b) What is the magnitude of  $D$  at  $875^\circ \text{C}$ ?*

T ( $^\circ \text{C}$ )	D ( $\text{m}^2/\text{s}$ )
650	$5.5 \times 10^{-16}$
900	$1.3 \times 10^{-13}$

