Chemical Engineering 378

Science of Materials Engineering

Lecture 10

Non Steady-State Diffusion

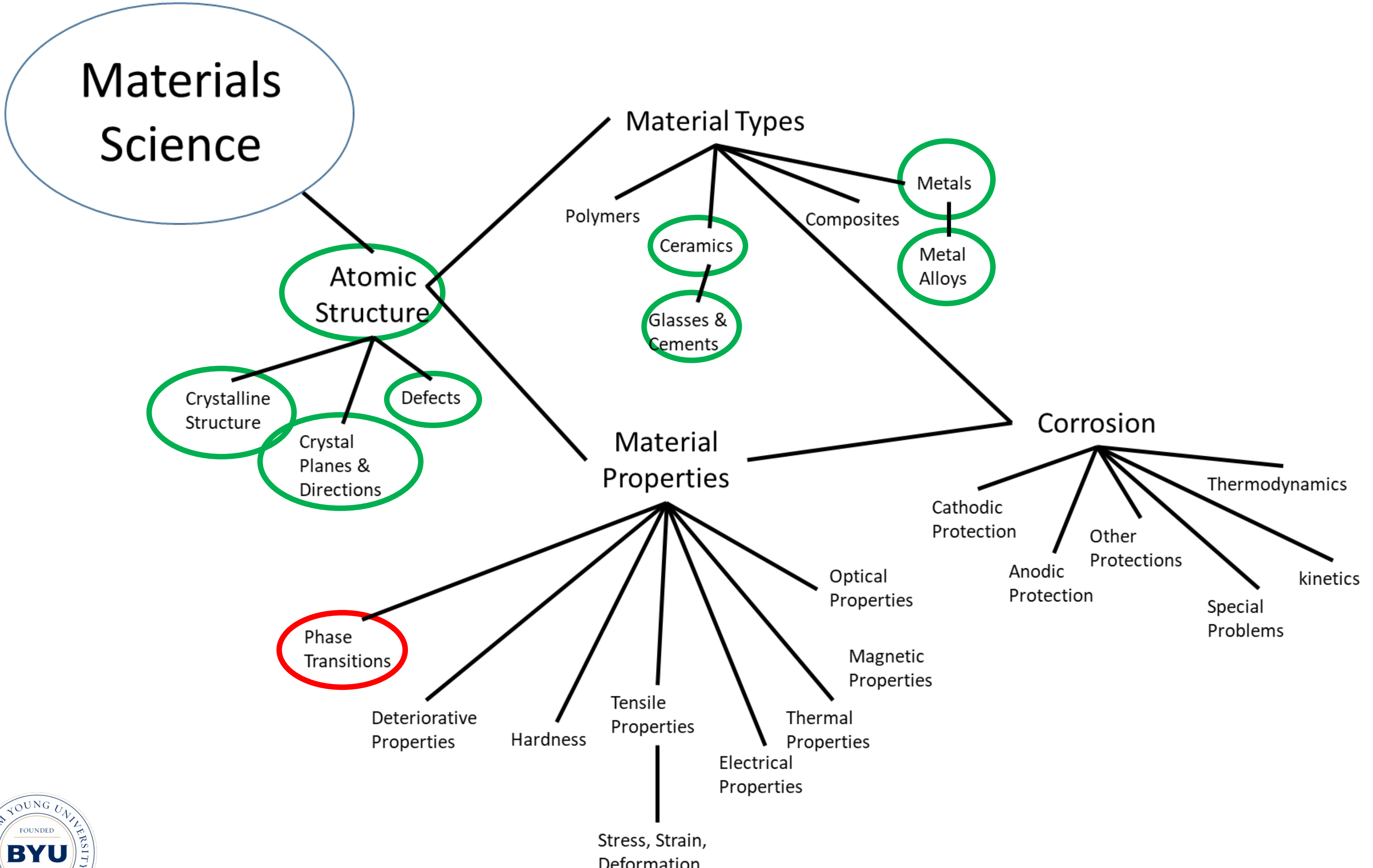
Spiritual Thought

"Many of us miss opportunity when it knocks because it comes to the door dressed in overalls and looks like work."

-President Thomas S. Monson

(quoting Thomas Edison)

Materials Roadmap



Open Ended Problem

OEP 4

Open Ended Problem #4

The Legend of Zelda

Group work okay, Due 10/4/23 at beginning of class

(Don't be afraid to "Google" for reasonable assumptions; just provide references!)

Hyrule has no gyms; Hyrule needs no gyms!

Besides this being one of the most epic games ever, the concept of getting stronger just from wearing a special pair of gloves is pretty awesome. Think of what we could accomplish if they were real? Now, the Hylians only said you “could live previously immovable stones”, but you all have one major advantage over the Hylians… you are material science EXPERTS! Given that, please calculate and quantify just how powerful the Titan’s Mitts are.

Species Continuity Equations

$$\frac{\partial C_A}{\partial t} + \vec{v}\nabla C_A = \nabla D \nabla C_A + R_A$$

Rectangular Coordinates:

$$\frac{\partial c_A}{\partial t} + \left(v_x \frac{\partial c_A}{\partial x} + v_y \frac{\partial c_A}{\partial y} + v_z \frac{\partial c_A}{\partial z} \right) = D_{AB}\left(\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2} \right) + R_A$$

Cylindrical Coordinates:

$$\frac{\partial c_A}{\partial t} + \left(v_r \frac{\partial c_A}{\partial r} + v_\theta \frac{1}{r}\frac{\partial c_A}{\partial \theta} + v_z \frac{\partial c_A}{\partial z} \right) = D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r \frac{\partial c_A}{\partial r} \right) + \frac{1}{r^2}\frac{\partial^2 c_A}{\partial \theta^2} + \frac{\partial^2 c_A}{\partial z^2} \right] + R_A$$

Spherical Coordinates:

$$\frac{\partial c_A}{\partial t} + \left(v_r \frac{\partial c_A}{\partial r} + v_\theta \frac{1}{r}\frac{\partial c_A}{\partial \theta} + v_\phi \frac{1}{r\sin\theta}\frac{\partial c_A}{\partial \phi} \right) =$$

$$D_{AB}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c_A}{\partial r} \right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial c_A}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 c_A}{\partial \phi^2} \right] + R_A$$

Non-steady State Diffusion

- The concentration of diffusing species is a function of both time and position $C = C(x,t)$
- For non-steady state diffusion, we seek solutions to Fick' s Second Law

Fick's Second Law

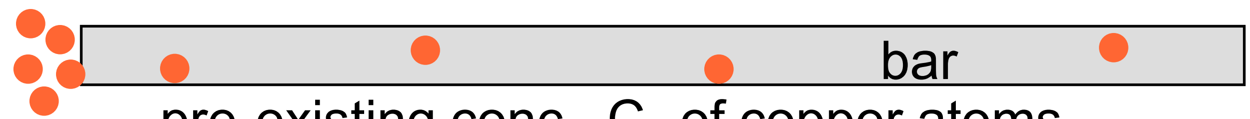
$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

This form of the equation assumes D is independent of concentration

Non-steady State Diffusion

- Consider the diffusion of copper into a bar of aluminum

Surface conc., C_S of Cu atoms



pre-existing conc., C_o of copper atoms

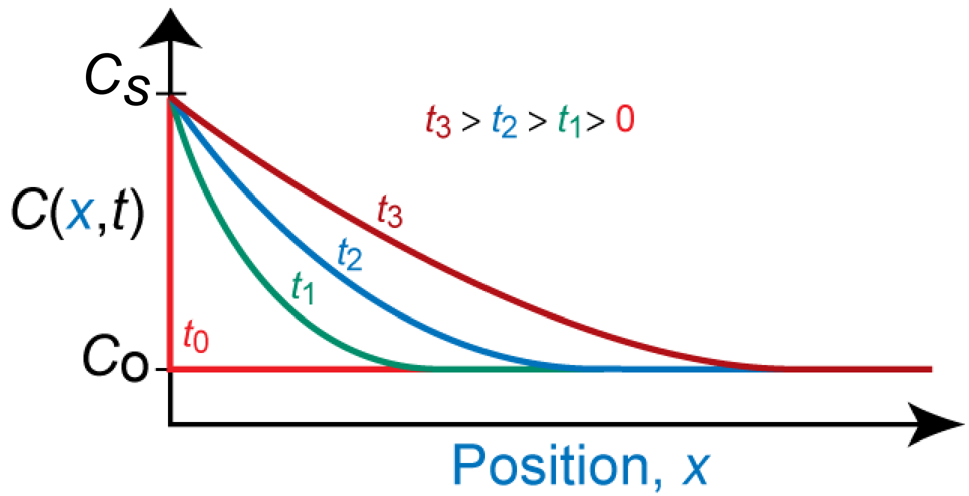


Fig. 5.4, Callister & Rethwisch 10e.

Boundary/Initial Conditions

at $t = 0$, $C = C_o$ for $0 \le x \le \infty$

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

$C = C_o$ for $x = \infty$

Non-steady State Diffusion (cont.)

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

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

erf(z) = error function

z and erf(z) values are given in Table 5.1

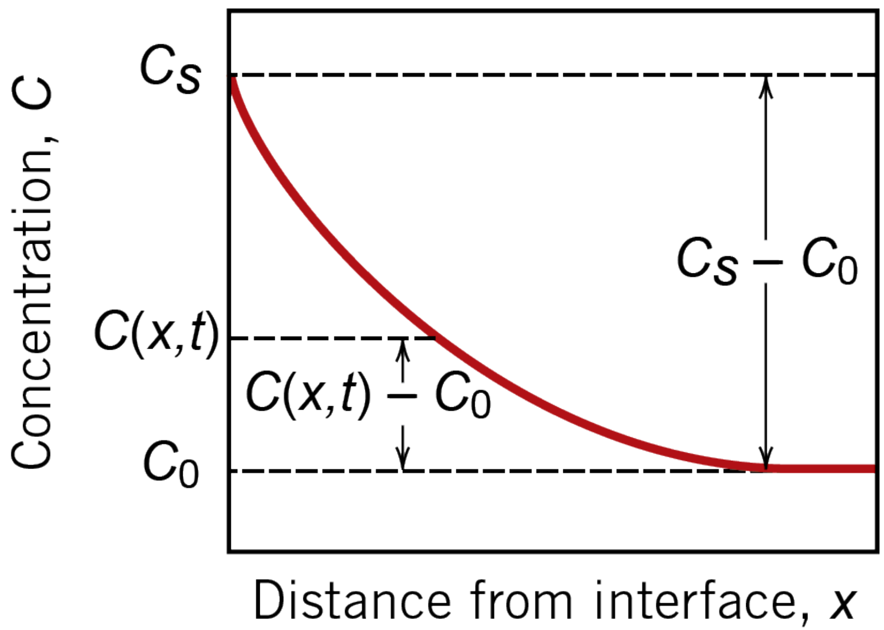


Fig. 5.5, Callister & Rethwisch 10e.

Table of Error Functions

z	*erf*(*z*)	*z*	*erf*(*z*)	*z*	*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

Non-steady State Diffusion

Example Problem

An FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere in which the surface carbon concentration is maintained 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 temperature at which the treatment was carried out.

Example Problem (cont.):

Solution: use Eqn. 5.5 $$\frac{C(x,t)-C_o}{C_s-C_o}=1-\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Data for problem tabulated as follows:

- t = 49.5 h
- x = 4 x 10^{-3} m
- C_x = 0.35 wt%
- C_s = 1.0 wt%
- C_o = 0.20 wt%

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

erf(z) = 0.8125

Example Problem (cont.):

We must now determine from Table 5.1 the value of z for which the error function is 0.8125. An interpolation is necessary as follows

z	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

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

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

Diffusion Data

Table 5.2 A Tabulation of Diffusion Data

Diffusing Species	*Host Metal*	$D_0(m^2/s)$	*Activation Energy Q_d* kJ/mol	*Activation Energy Q_d* eV/atom	*Calculated Value* $T(°C)$	*Calculated Value* $D(m^2/s)$
Fe	α-Fe (BCC)	2.8×10^{-4}	251	2.60	500	3.0×10^{-21}
					900	1.8×10^{-15}
Fe	γ-Fe (FCC)	5.0×10^{-5}	284	2.94	900	1.1×10^{-17}
					1100	7.8×10^{-16}
C	α-Fe	6.2×10^{-7}	80	0.83	500	2.4×10^{-12}
					900	1.7×10^{-10}
C	γ-Fe	2.3×10^{-5}	148	1.53	900	5.9×10^{-12}
					1100	5.3×10^{-11}
Cu	Cu	7.8×10^{-5}	211	2.19	500	4.2×10^{-19}
Zn	Cu	2.4×10^{-5}	189	1.96	500	4.0×10^{-18}
Al	Al	2.3×10^{-4}	144	1.49	500	4.2×10^{-14}
Cu	Al	6.5×10^{-5}	136	1.41	500	4.1×10^{-14}
Mg	Al	1.2×10^{-4}	131	1.35	500	1.9×10^{-13}
Cu	Ni	2.7×10^{-5}	256	2.65	500	1.3×10^{-22}

Source: E. A. Brandes and G. B. Brook (Editors), *Smithells Metals Reference Book*, 7th edition, Butterworth-Heinemann, Oxford, 1992.

Example Problem (cont.):

- To solve for the temperature at which D has the above value, we use a rearranged form of Equation 5.9a

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

From Table 5.2, for diffusion of C in FCC Fe

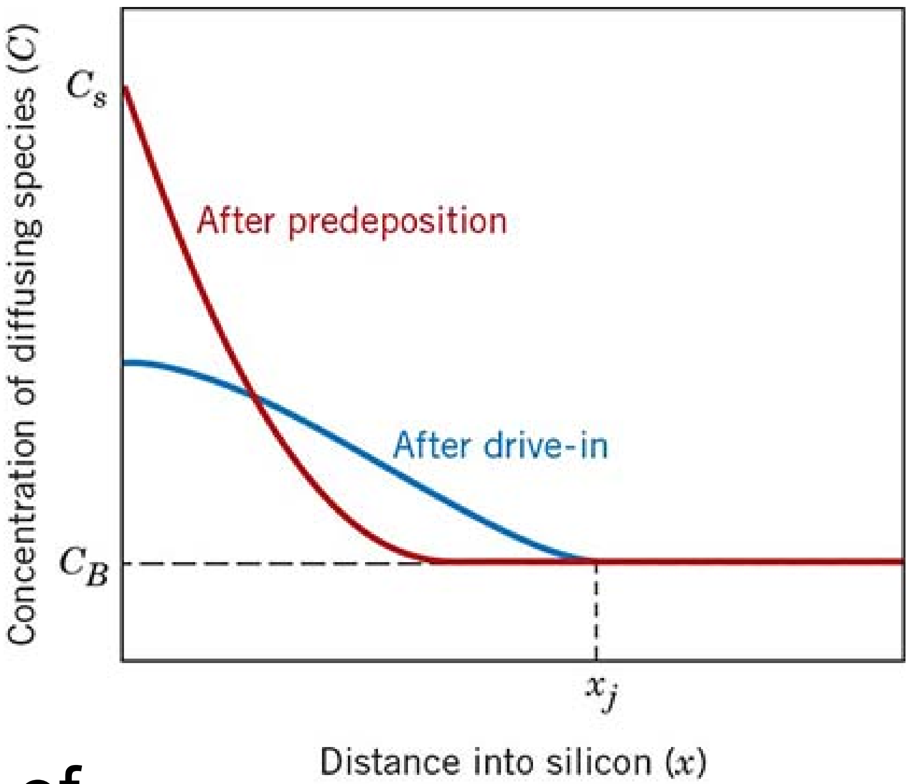
$D_o = 2.3 \times 10^{-5}\ \text{m}^2/\text{s}$ $Q_d = 148{,}000\ \text{J/mol}$

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

$T = 1300\ \text{K} = 1027°\ \text{C}$

Semiconductors

- 2 stages:
  - Predeposition (~1100° C)
  - Drive-in (~1200° C)
- Assuming thin layer:
- $C(x,t) = \frac{Q_0}{\sqrt{\pi D t}} e^{\left(-\frac{x^2}{4Dt}\right)}$
  - Q_0 = total impurities (# of atoms/unit area)
- $Q_0 = 2C_s\sqrt{\frac{D_p t_p}{\pi}}$



Summary

- Solid-state diffusion is mass transport within solid materials by stepwise atomic motion
- Two diffusion mechanisms
  - Vacancy diffusion
  - Interstitial diffusion
- Fick's First Law of Diffusion $$J = -D\frac{dC}{dx}$$
- Fick's Second Law of Diffusion
  - non-steady state diffusion $$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$
- Diffusion coefficient
  - Effect of temperature $$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$