



# EMA5001 Lecture 8

## Review for Diffusion



# Expectations about Diffusion (1)

- Can name major categories and mechanisms of diffusion
- Can give practical examples of applications of diffusion
- Understand the similarity & difference between down-hill and up-hill diffusion
- Remember Fick's 1<sup>st</sup> and 2<sup>nd</sup> Law and can derive them based on 1-D geometry
- Can derive thermo activation of diffusion and calculate activation energy and frequency factor, if given diffusion data at different temperatures
- Can derive concentration profile for steady state diffusion in 1-D
- Can name major example solutions Fick's 2<sup>nd</sup> Law and assumptions (no need to remember the math)
- Remember expression of diffusion length and can explain how its significance



# Expectations about Diffusion (2)

- Understand the relationship between self diffusion and vacancy diffusion coefficients
- Understand the significance of Kirkendall effect
- Understand Darken's equations
- Can derive the relationship between diffusion coefficient and mobility
- Can explain the relationship between tracer diffusion, intrinsic diffusion, and interdiffusion coefficients
- Understand why Matano analysis is needed and can explain the significance of Matano interface
- Can describe how diffusion coefficients are obtained in experiments
- Can derive relationship between apparent diffusion coefficient for diffusion through multi-crystalline or single crystalline materials with dislocations
- Can draw the concentration profile for reaction diffusion involving multi-phases



# Diffusion Coefficient of Carbon in $\alpha$ -Fe vs. $\gamma$ -Fe (1)

❑ Diffusion coefficient of Carbon in  $\alpha$ -Fe (BCC) is ~100 times higher than in  $\gamma$ -Fe (FCC) at 910 °C

Crystal structure	$D_0$ (mm <sup>2</sup> /s)	Q (kJ/mol)
C in $\alpha$ -Fe (BCC)	2	84.1
C in $\gamma$ -Fe (FCC)	20	142

James P Schaffer, et al. *The Science & Design of Engineering Materials*, 2<sup>nd</sup> Ed, McGraw-Hill, (1999), p. 131

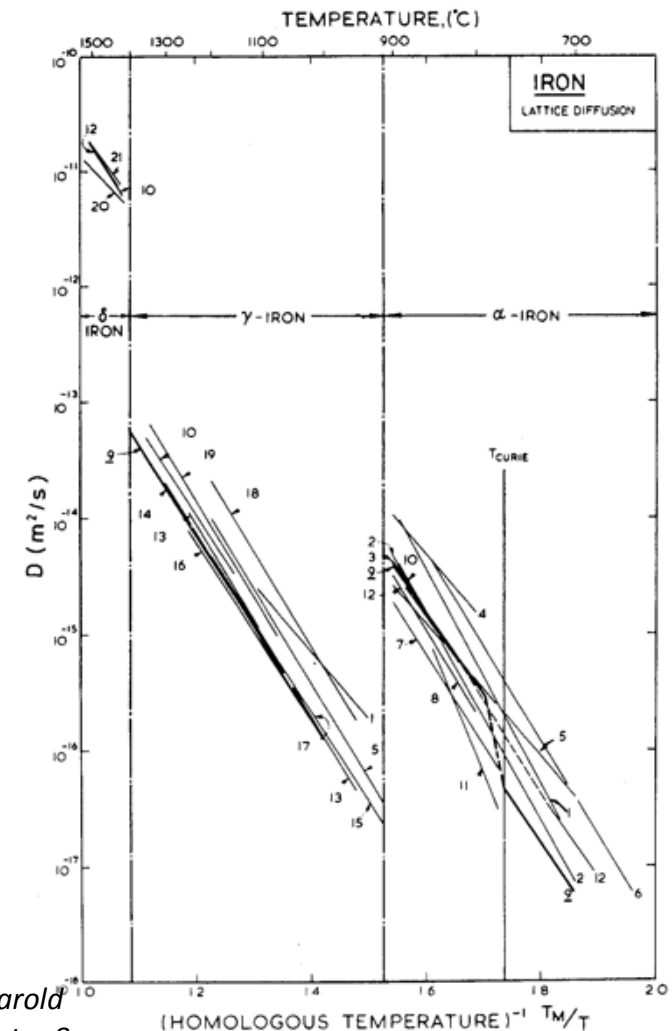
❑ “Closer packing” for  $\gamma$ -Fe is cited

- “The reason for this huge difference lies in the fact that the bcc structure is more open and the diffusion process requires less lattice distortion (enthalpy or thermodynamically favored).”

<http://www.eng.utah.edu/~lzung/images/lecture-7-experimental-measurement-interdiffusion-coefficient-kirkendall-effect.pdf>

*Deformation-Mechanism Maps, The Plasticity and Creep of Metals and Ceramics*, by Harold J Frost, Dartmouth College, USA, and Michael F Ashby, Cambridge University, UK. Chapter 8

<http://engineering.dartmouth.edu/defmech/>





# Diffusion Coefficient of Carbon in $\alpha$ -Fe vs. $\gamma$ -Fe (2)

## ❑ Size & Number of Interstitials in BCC & FCC structures

Crystal structure	Packing density	Ratio of radius of largest tetrahedral atom to host	Ratio of radius of largest <u>octahedral</u> atom to host	Number of tetrahedral site per unit cell (per host atoms)	Number of Octahedral site per unit cell (per host atoms)
BCC	0.68	0.291	0.155	12 (6)	6 (3)
FCC	0.74	0.225	0.414	8 (2)	4 (1)

*James P Schaffer, etc. The Science & Design of Engineering Materials, 2<sup>nd</sup> Ed, McGraw-Hill, (1999), p. 82 & 87*

## ❑ Carbon occupy **octahedral** sites in both $\alpha$ -Fe (BCC) and $\gamma$ -Fe (FCC) despite the size of octahedral site is much smaller in $\alpha$ -Fe (BCC)

“at least 85% of the carbon atoms occupy octahedral interstices”

*G.K. Williamson, “X-ray evidence for the interstitial position of carbon in  $\alpha$ - iron,” Acta Cryst. (1953), p.361*

## ❑ The **number (density) of octahedral interstitials** per unit cell (or per atom) is much larger for $\alpha$ -Fe (BCC) than for $\gamma$ -Fe (FCC)



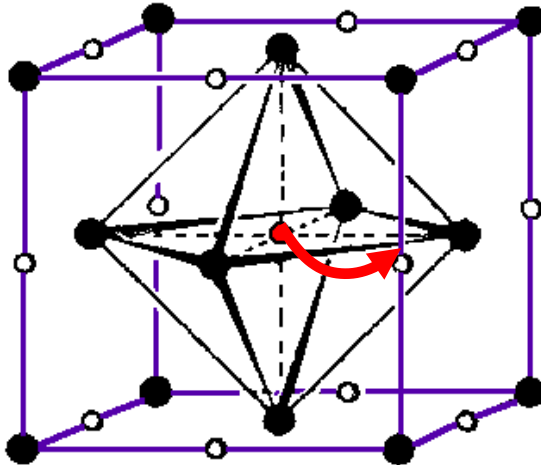
# Diffusion Coefficient of Carbon in $\alpha$ -Fe vs. $\gamma$ -Fe (3)

□ The jumping distance in  $\alpha$ -Fe (BCC) is much shorter than in  $\gamma$ -Fe (FCC)

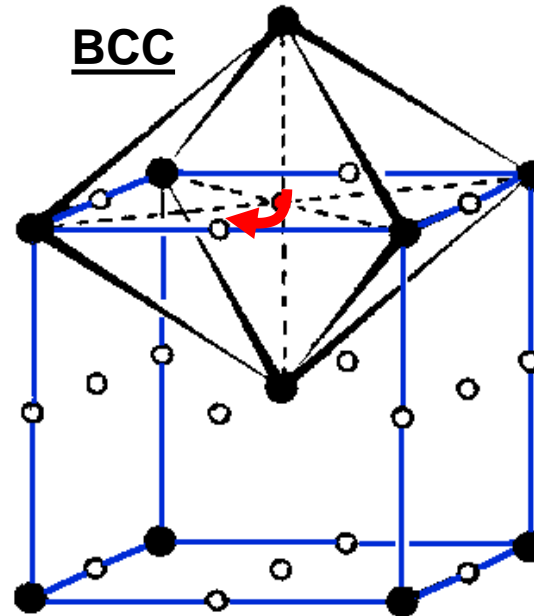
▪ FCC:  $\lambda_C^\gamma = \frac{1}{\sqrt{2}} a_{\gamma\text{-Fe}} = \frac{1}{\sqrt{2}} \cdot \frac{4}{\sqrt{2}} r_{\text{Fe}} = 2r_{\text{Fe}}$

▪ BCC:  $\lambda_C^\alpha = \frac{1}{2} a_{\alpha\text{-Fe}} = \frac{1}{2} \cdot \frac{4}{\sqrt{3}} r_{\text{Fe}} = \frac{2}{\sqrt{3}} r_{\text{Fe}} = \frac{1}{\sqrt{3}} \lambda_C^\gamma$

FCC



BCC



[http://www.tf.uni-kiel.de/matwis/amat/def\\_en/kap\\_1/illustr/t1\\_3\\_3.html](http://www.tf.uni-kiel.de/matwis/amat/def_en/kap_1/illustr/t1_3_3.html)



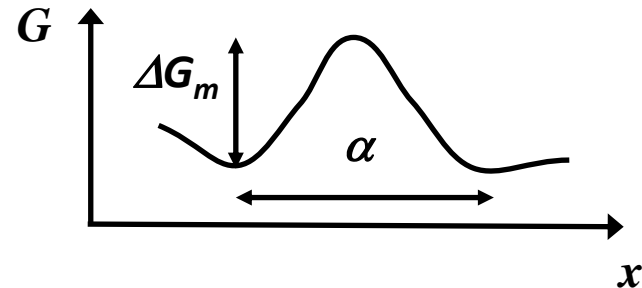
# Successful Jump Frequency, Vibration Frequency

## ❑ Thermal vibration frequency

$\nu$  - Thermal vibration frequency

## ❑ (Successful) Jump frequency

$$\Gamma_B = \nu \exp\left(-\frac{\Delta G_m}{RT}\right)$$



## ❑ In text book, p. 72-73, (successful) jump frequency was written slightly differently:

$$\Gamma_B = z \nu' \exp\left(-\frac{\Delta G_m}{RT}\right)$$

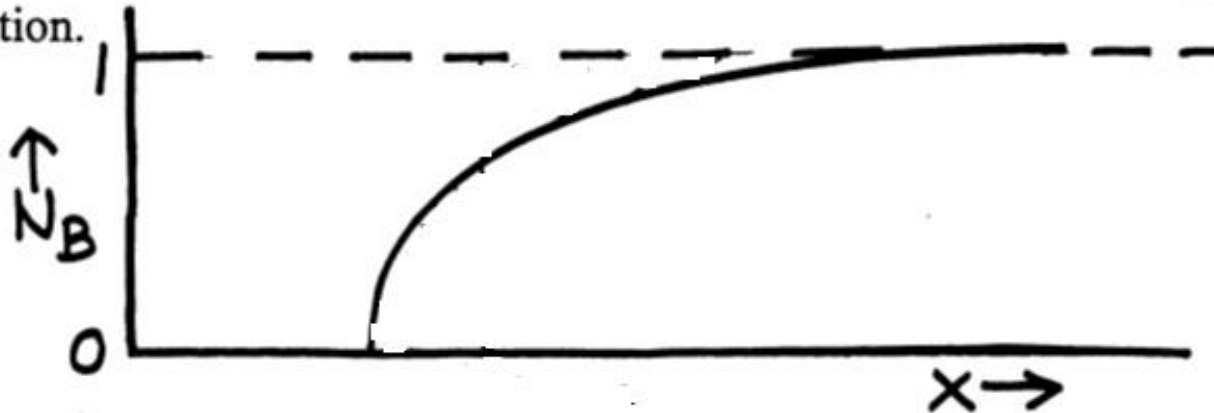
- $\nu'$  is for “in the  $x$  direction it makes  $\nu'$  attempts per second to jump...” (i.e., vibration frequency in  $x$  direction)
- $z$  is the number of such sites (e.g., acceptable interstitials) in 3D
- Naturally,  
$$\nu = z \nu'$$
- It does not help further understanding, and we did not adopt it here



# Concentration Profile & Darken's Equation

**Problem:** The interdiffusion composition profile in an infinite couple (made of pure A and pure B) is shown below. Further, it is given that:

- the molar volume of the system is constant, and
- the intrinsic diffusion coefficients of A and B are constant with respect to composition.



- Mark the location of the Matano interface on the diagram shown. Provide a brief explanation for your answer.
- What is the value of the interdiffusion coefficient at  $N_B = 0$ ?
- Sketch how the interdiffusion coefficient varies with  $N_B$ . Explain.
- Which direction the Kirkendall markers will move and why?

<http://www.matsceng.ohio-state.edu/~gupta/mse732/quiz2.pdf>





# Movement for Kirkendall Interface

- Displacement of Kirkendall Interface  $l$  satisfy  $l^2 = At$ , if at that time  $t$ , the interface has moved  $l$ , what is the velocity of the Kirkendall interface ?

$$l^2 = At$$

$$u = \frac{dl}{dt} = \frac{d(\sqrt{At})}{dt} = \frac{\sqrt{A}}{2\sqrt{t}} = \frac{\sqrt{At}}{2t} = \frac{l}{2t} \neq \frac{l}{t}$$

$$2l dl = A dt$$

$$u = \frac{dl}{dt} = \frac{A}{2l}$$



# Darken's Equation & Flux due to Brownian Motion & Interface Movement

Consider a binary alloy (components A and B). Fluxes are measured at a certain point where the composition is 60 mole % B and the molar volume is  $0.20 \text{ m}^3/\text{mol}$ . The values of the measured fluxes for the two components are:  $100 \text{ moles} / (\text{m}^2 \text{ S})$  for component A and  $60 \text{ moles} / (\text{m}^2 \text{ S})$  for component B. Calculate

- the interdiffusion flux of component B in the molar reference frame, and
- the velocity of the molar reference frame with respect to the lab reference frame.

**□ The problem and the original solution given is awkward and, most likely, wrong.**

I would use

$$J_A' = 100 \text{ mol}/(\text{m}^2\text{sec}); J_B' = -60 \text{ mol}/(\text{m}^2\text{sec})$$

$$C_0 = 5 \text{ mol}/\text{m}^3$$

$$C_B = 5 \times 60\% = 3 \text{ mol}/\text{m}^3; C_A = 5 \times 40\% = 2 \text{ mol}/\text{m}^3$$

$$J_A = J_A' + uC_A; J_B = J_B' + uC_B$$

$$J_A + J_B = 0$$

Therefore,

$$J_A = 84 \text{ mol}/(\text{m}^2\text{sec})$$

$$u = -8 \text{ m}/\text{sec}$$

<http://www.matsceng.ohio-state.edu/~gupta/mse732/quiz1.pdf>



# Porter 3<sup>rd</sup> Exercise 2.1

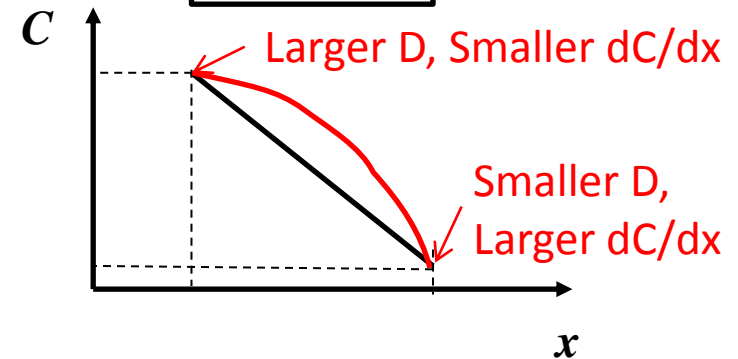
## □(a) Steady state → constant flux

- Assuming constant diffusion coefficient → Linear profile
- Changing diffusion coefficient → Curve

Surface 1 for carburization



Surface 2 for decarburization



## □(b) D changes with concentration

$$J_B = -D_B \frac{\partial C_B}{\partial x}$$

Constant flux

$$J_B = -D_B(x = x_1) \frac{\partial C_B}{\partial x} \Big|_{x=x_1} = -D_B(x = x_2) \frac{\partial C_B}{\partial x} \Big|_{x=x_2}$$

$$\frac{\frac{\partial C_B}{\partial x} \Big|_{x=x_1}}{\frac{\partial C_B}{\partial x} \Big|_{x=x_2}} = \frac{D_B(x = x_2)}{D_B(x = x_1)} = \frac{2.5}{7.7} = 0.32$$



# Porter 3<sup>rd</sup> Exercise 2.1

Using average diffusion coefficient  $D = 5.1 \times 10^{-11} \text{ m}^2/\text{sec}$

Flux

$$J_B = -D_B \frac{\partial C_B}{\partial x} = 5.1 \times 10^{-11} \text{ m}^2 / \text{s} \frac{(1.4\% - 0.15\%) / 0.8\% \times 60 \text{ kg} / \text{m}^3}{0.002 \text{ m}}$$

$$J_B = 2.4 \times 10^{-6} \text{ kgm}^{-2} \text{ s}^{-1}$$

The answer given in the book is too complicated and end up with the same answer



# Porter 3<sup>rd</sup> Exercise 2.3

□ Concentration profile for “spin on dopant” type

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

At constant time, we have

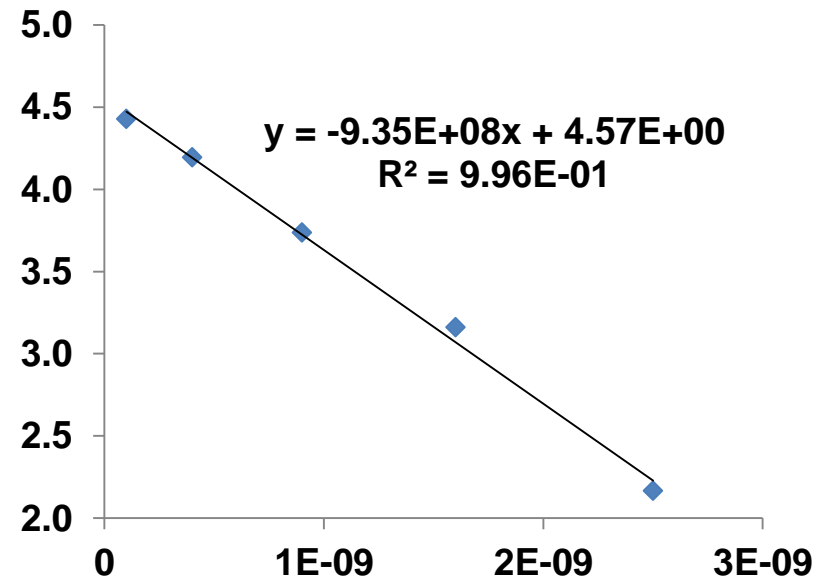
$$\ln C_B(x) = \ln \frac{N}{\sqrt{\pi Dt}} - \frac{x^2}{4Dt}$$

Plotting  $\ln C_B$  versus  $x^2$ ,  
slope will be  $-1/(4Dt)$

Plotting the data, we have

$$-\frac{1}{4Dt} = -9.35 \times 10^8$$

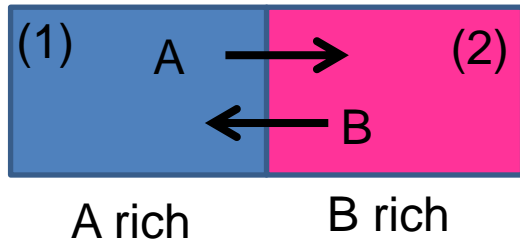
$$D = \frac{1}{4 \times 24 \times 3600 \times 9.35 \times 10^8} = 3.1 \times 10^{-15} \text{ m}^2 / \text{s}$$





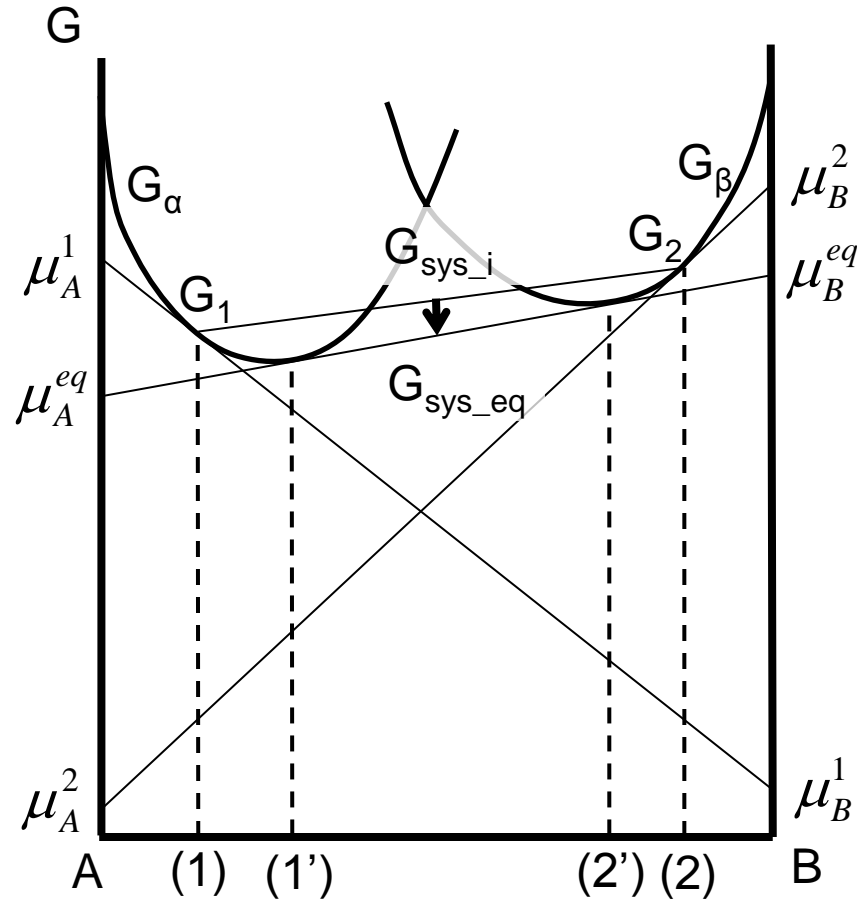
# Porter 3<sup>rd</sup> Exercise 2.6

Free energy → Chemical potential



$$\mu_A^{1'} = \mu_A^{2'} = \mu_A^{eq}$$

$$\mu_B^{1'} = \mu_B^{2'} = \mu_B^{eq}$$





# Porter 3<sup>rd</sup> Exercise 2.7

## □ Interdiffusion coefficient

$$\tilde{D} = X_{Cu} D_{Zn} + X_{Zn} D_{Cu} = 4.5 \times 10^{-13} m^2 / sec$$

$$u = (D_{Zn} - D_{Cu}) \frac{\partial X_{Zn}}{\partial x} = 2.6 \times 10^{-8} mm / sec$$

$$X_{Zn} = 0.22 \quad X_{Cu} = 0.78 \quad \frac{\partial X_{Zn}}{\partial x} = 0.089 / mm$$

$$0.78 D_{Zn} + 0.22 D_{Cu} = 4.5 \times 10^{-13} m^2 / sec$$

$$D_{Zn} - D_{Cu} = \frac{2.6 \times 10^{-8} mm / sec}{0.089 / mm} = 2.92 \times 10^{-13} m^2 / sec$$

$$D_{Zn} = 5.1 \times 10^{-13} m^2 / sec$$

$$D_{Cu} = 2.2 \times 10^{-13} m^2 / sec$$

As Zn concentration increases, all three diffusion coefficients increase due to lower melting point of Zn