



EMA5001 Lecture 5

Diffusion in Substitutional Alloys

- Kirkendall Effect & Darken Equations**

Kirkendall Effect

Experiment

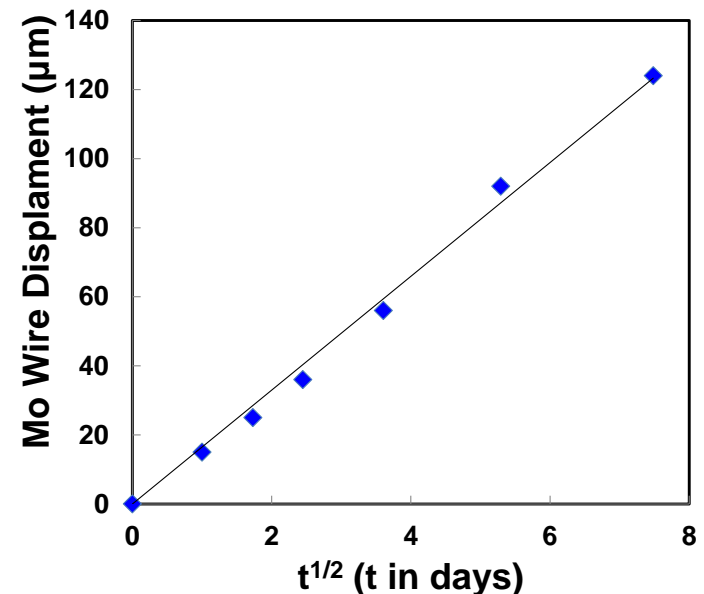
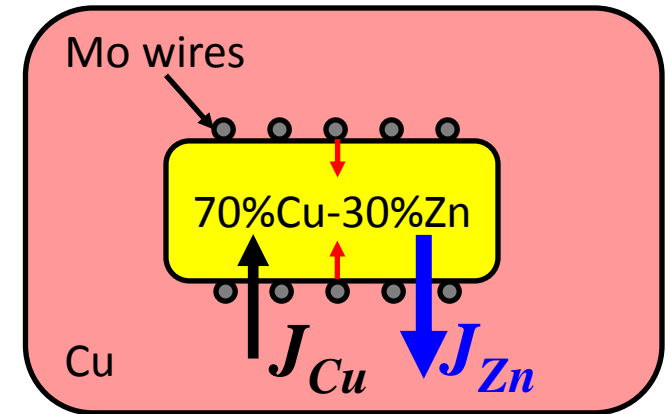
- α -Brass (70%Cu-30%Zn) winded with Mo wires, then electroplate with pure Cu. Anneal/diffusion at 785 °C
- Mo wires are marker, not soluble
- Cu-Zn substitutional solid solution

Observations

- Mo wires move towards inside; its displacement follow $t^{0.5}$, larger than expected from the change due to atom size difference
- The interface between brass and Cu moves together with the Mo wires

Implications

- $|J'_{Zn}| > |J'_{Cu}|$ w.r.t. the *moving* interface
- Diffusion through *vacancy mechanism*



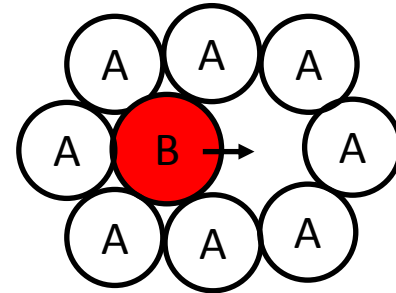
A. D. Smigelskas and E. O. Kirkendall, *Trans. Am. Inst. Min. Met. Eng.* 171, 130 (1947)



Diffusion Flux Relative to Lattice Plane

□ Difference in atoms of A vs. B

Different in size, valence state, melting point, etc. → Difference in diffusion rate or diffusion coefficient



□ Atom Flux with Respect to Lattice

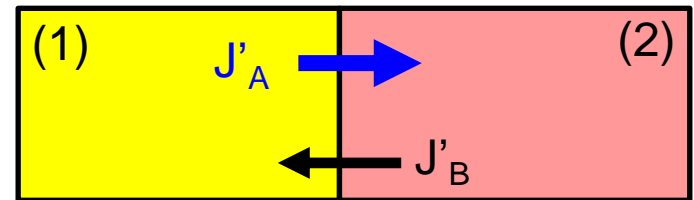
For diffusion of A and B **with respect to a lattice plane (a moving coordinate)**, which is **Brownian in nature**, using Fick's 1st Law,

$$J'_A = -D_A \frac{\partial C_A}{\partial x'}$$

$$J'_B = -D_B \frac{\partial C_B}{\partial x'}$$

J'_A and J'_B are fluxes of atom A and B **across a given lattice plane**

D_A and D_B are defined as **partial diffusion coefficient** or **intrinsic diffusion co-efficient**

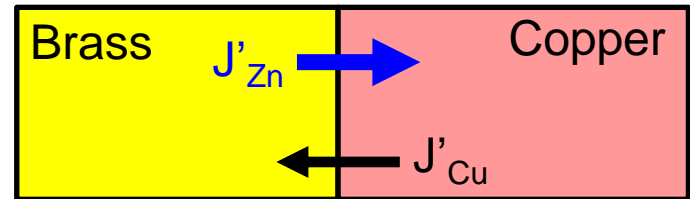




Movement of the Interface

□ What happens if interface does NOT move?

- $|J'_{Zn}| > |J'_{Cu}|$
 - Interface does not move
- Excess vacancy will form in brass (Zn rich side) → Vacancy will tend to diffuse from brass to copper following Fick's 1st law



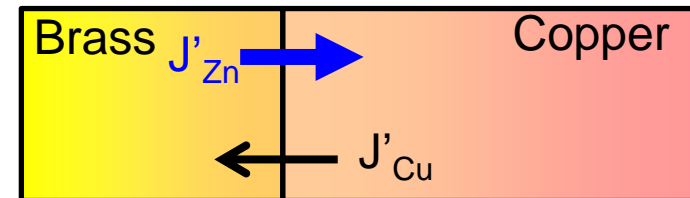
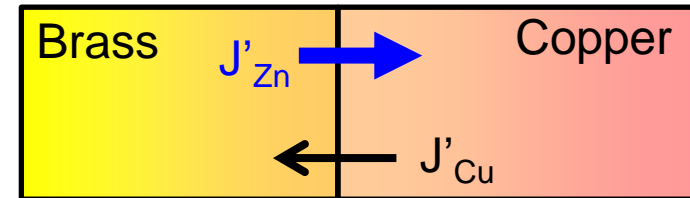
□ Diffusional flux of vacancy leads to movement of interface

Assuming total number of atoms per unit volume is constant of C_0

$$C_A + C_B = C_0$$

We have

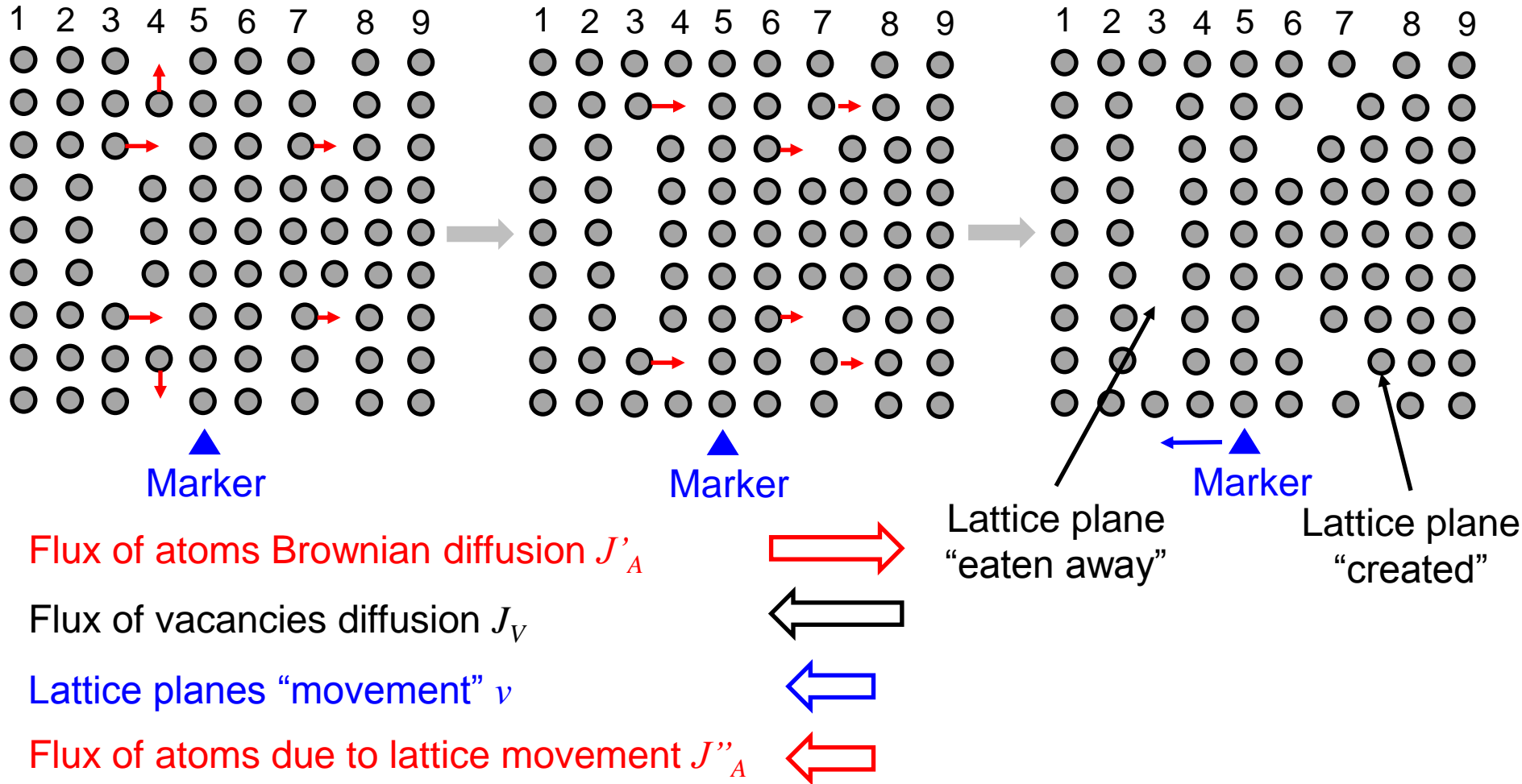
$$\frac{\partial C_A}{\partial x'} = \frac{\partial (C_0 - C_B)}{\partial x'} = -\frac{\partial C_B}{\partial x'}$$





Movement of Lattice Planes as a Result of Flux of Vacancies

□ Net flux of vacancy leads to movement of lattice planes





Mathematic Derivation of Flux of Vacancies

□ Vacancy flux

For a flux of atoms to occur, there is a equal flux of vacancies in the opposite direction.

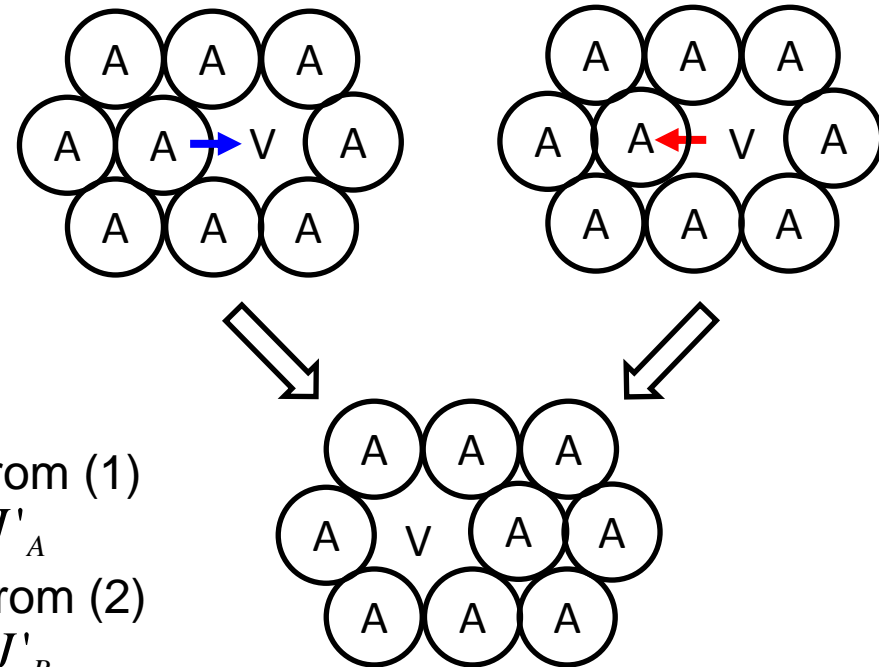
Assuming $D_A > D_B$
 $|J'_A| > |J'_B|$

- Vacancy flux due to diffusion of atom A from (1) to (2) with respect to the lattice plane $-J'_A$
- Vacancy flux due to diffusion of atom B from (2) to (1) with respect to the lattice plane $-J'_B$
- The net flux of vacancies $J'_v = (-J'_A) + (-J'_B) = -J'_A - J'_B$

Knowing $J'_A = -D_A \frac{\partial C_A}{\partial x'}$ $J'_B = -D_B \frac{\partial C_B}{\partial x'} = D_B \frac{\partial C_A}{\partial x'}$

We have

$$J'_v = -\left(-D_A \frac{\partial C_A}{\partial x'}\right) - \left(D_B \frac{\partial C_A}{\partial x'}\right) = (D_A - D_B) \frac{\partial C_A}{\partial x'}$$





Flux of Atoms as a Result of Lattice Plane Movement

□ Continue from p. 5

Vacancy net flux with respect to the lattice plane

$$J'_v = -\left(-D_A \frac{\partial C_A}{\partial x'}\right) - \left(D_B \frac{\partial C_A}{\partial x'}\right) = (D_A - D_B) \frac{\partial C_A}{\partial x'}$$

Define the **velocity of that lattice plane movement** as a result of vacancy flux as u ,

$$u = \frac{J'_v}{C_0} = \frac{(D_A - D_B) \frac{\partial C_A}{\partial x'}}{C_0} = (D_A - D_B) \frac{\partial \left(\frac{C_A}{C_0}\right)}{\partial x'} = (D_A - D_B) \frac{\partial X_A}{\partial x'}$$

For fixed time t and velocity, the relationship between two coordinates is $x = x' + ut$

$$u = (D_A - D_B) \frac{\partial X_A}{\partial x'} = (D_A - D_B) \frac{\partial X_A}{\partial x} \cdot \frac{\partial x}{\partial x'} = (D_A - D_B) \frac{\partial X_A}{\partial x}$$

We have

$$u = (D_A - D_B) \frac{\partial X_A}{\partial x}$$

Darken's Equation

Flux of atom A due to lattice movement $J''_A = C_A u$ Note for $D_A > D_B$, $u < 0$



Total Flux with Respect to External Coordinates

□ Total flux of A with respect to external coordinates (sample end surface)

Consists of two terms

- **Diffusive flux** of A due to diffusion relative to the **lattice** $J'_A = -D_A \frac{\partial C_A}{\partial x'} = -D_A \frac{\partial C_A}{\partial x}$
- Flux due to relative velocity of the lattice to the external coordinates $J''_A = C_A u$

The total flux

$$J_A = J'_A + C_A u$$

Given lattice movement velocity $u = (D_A - D_B) \frac{\partial X_A}{\partial x}$

We have

$$\begin{aligned} J_A &= -D_A \frac{\partial C_A}{\partial x} + \left[(D_A - D_B) \frac{\partial X_A}{\partial x} \right] C_A = -D_A \frac{\partial C_A}{\partial x} + (D_A - D_B) \frac{\partial C_A}{\partial x} X_A \\ &= -(D_A - D_A X_A + D_B X_A) \frac{\partial C_A}{\partial x} = -[D_A (1 - X_A) + D_B X_A] \frac{\partial C_A}{\partial x} = -(D_A X_B + D_B X_A) \frac{\partial C_A}{\partial x} \end{aligned}$$



Inter-diffusion Coefficient

□ Continue from p. 7

$$J_A = -(D_A X_B + D_B X_A) \frac{\partial C_A}{\partial x}$$

Define **inter-diffusion coefficient**

$$\tilde{D} = D_A X_B + D_B X_A$$

Darken's Equation

$$\tilde{D} \neq D_A \neq D_B$$

The **total flux of A with respect to specimen end surface** (or external coordinates)

$$J_A = -\tilde{D} \frac{\partial C_A}{\partial x}$$

Similarly,

$$J_B = -\tilde{D} \frac{\partial C_B}{\partial x} = \tilde{D} \frac{\partial C_A}{\partial x}$$

And

$$J_B = -J_A$$

NO (large) change in local density

Fick's 2nd Law

$$\frac{\partial C_A}{\partial t} = -\frac{\partial J_A}{\partial x}$$

becomes

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



Considerations on Inter-Diffusion Coefficient

□ Inter-diffusion coefficient

- Measured in diffusion couple experiments for substitutional alloys
- Substitution diffusion of atoms often much slower than interstitial diffusion, e.g.,
For BCC α -Fe diffusion at 1000 K
 - Diffusion coefficient of carbon atom (interstitial diffusion) is $81 \mu\text{m}^2/\text{sec}$
 - Self diffusion coefficient of iron atom is $6.0 \times 10^{-5} \mu\text{m}^2/\text{sec}$

□ Inter-diffusion depends on crystal structure

- Interstitial atoms
Carbon diffusion in α -Fe vs. γ -Fe at 910 °C: $D_C^\alpha / D_C^\gamma = 100$
- Substitutional atoms
Fe self diffusion in α -Fe vs. γ -Fe at 850 °C: $D_{Fe}^\alpha / D_{Fe}^\gamma = 100$

□ Inter-diffusion in dilute binary alloys

Dilute alloy of B in A, $\tilde{D} = D_A X_B + D_B X_A$

When $X_B \rightarrow 0$

$$\tilde{D} \approx D_B$$



Mobility & Description of Atom Flux by Drift due to a Driving Force (Potential)

□ An alternative way of describing diffusive flux of atoms

Net drift velocity v **superimposed on random jumping** due to a driving force/potential

Intrinsic diffusive flux of B (with respect to a lattice plane) is related to drift velocity as

$$J_B = v_B C_B$$

Drift velocity is proportional to local gradient of chemical potential, i.e.,

$$v_B = -M_B \frac{\partial \mu_B}{\partial x'} = -M_B \frac{\partial \mu_B}{\partial x}$$

Where M_B is the atomic mobility

Therefore, flux of B due to the driving force is

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x}$$



Mobility & Description of Atom Flux by Drift due to a Driving Force (Potential)

□ Continue from p. 11

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x}$$

Chemical potential for B is $\mu_B = \mu_B^0 + RT \ln a_B = \mu_B^0 + RT \ln(X_B \gamma_B)$

a_B , X_B , and γ_B is the activity, molar fraction, and activity coefficient of B, respectively

$$\mu_B = \mu_B^0 + RT \ln X_B + RT \ln \gamma_B$$

Therefore,

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x} = -M_B C_B \frac{\partial \mu_B}{\partial X_B} \cdot \frac{\partial X_B}{\partial x}$$

in which

$$\frac{\partial \mu_B}{\partial X_B} = RT \left(\frac{1}{X_B} + \frac{\partial \ln \gamma_B}{\partial X_B} \right) = \frac{RT}{X_B} \left(1 + \frac{\partial \ln \gamma_B}{\frac{\partial X_B}{X_B}} \right) = \frac{RT}{X_B} \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right)$$

$$\frac{\partial X_B}{\partial x} = \frac{\partial \left(\frac{C_B}{C_A + C_B} \right)}{\partial x} = \frac{1}{C_A + C_B} \cdot \frac{\partial C_B}{\partial x} \quad \text{as } (C_A + C_B) \text{ is a constant}$$



Mobility & Description of Atoms Flux by Drift due to a Driving Force (Potential)

□ Continue from p.12

$$\frac{\partial \mu_B}{\partial X_B} = \frac{RT}{X_B} \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right) \quad \frac{\partial X_B}{\partial x} = \frac{1}{C_A + C_B} \cdot \frac{\partial C_B}{\partial x}$$

Therefore, the flux of solute B

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial X_B} \cdot \frac{\partial X_B}{\partial x}$$

$$J_B = -M_B C_B \left[\frac{RT}{X_B} \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right) \right] \cdot \left[\frac{1}{C_A + C_B} \cdot \frac{\partial C_B}{\partial x} \right]$$

Rearrange, we have

$$J_B = -M_B RT \frac{1}{X_B} \cdot \frac{C_B}{C_A + C_B} \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right) \frac{\partial C_B}{\partial x}$$

$$J_B = -M_B RT \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right) \frac{\partial C_B}{\partial x}$$



Mobility & Diffusion Coefficient – Einstein Relationship

□ Continue from p. 13

$$J_B = -M_B RT \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right) \frac{\partial C_B}{\partial x}$$

Compare with Fick's 1st Law for **intrinsic** diffusion: $J_B = -D_B \frac{\partial C_B}{\partial x}$

We have

$$D_B = M_B RT \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right)$$

**Relationship Between Intrinsic
Diffusion Coefficient & Mobility**

For ideal solution or dilute solution (i.e, when $X_B \rightarrow 0$), γ_B is a constant, $\frac{\partial \ln \gamma_B}{\partial \ln X_B} = 0$

It is simplified as

$$D_B = M_B RT$$



Thermodynamic Factor

□ Intrinsic diffusion coefficient

$$D_B = M_B RT \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right)$$

□ For tracer element

Assuming the same mobility, we have $D_B^* = M_B^* RT = M_B RT$

Define **thermodynamic factor**

$$F = 1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} = 1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A} = \frac{X_A X_B}{RT} \cdot \frac{d^2 G}{dX^2}$$

We have
$$D_B = M_B RT \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right) = F D_B^*$$

Similarly,

$$D_A = F D_A^*$$

Interdiffusion coefficient
$$\tilde{D} = (D_A X_B + D_B X_A) = F (D_A^* X_B + D_B^* X_A)$$



D_B^* vs. D_B vs. \tilde{D}

- D_B^* **Tracer** diffusion coefficient (or **Self**-diffusion coefficient)

For diffusion in chemically **uniform** alloy/solution $D_B^* = M_B^* RT = M_B RT$

- D_B **Intrinsic** diffusion coefficient (or **partial** diffusion coefficient)

Intrinsic diffusion coefficient D_B is for Brownian diffusion of atoms in an alloy/solid solution **with concentration gradient** with respect to a lattice plane

$$D_B = M_B RT \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right) = \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \right) D_B^*$$

Define thermodynamic factor

$$F = 1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} \quad D_B = F D_B^*$$

For dilute solution (when $X_B \rightarrow 0$) or ideal solution γ_B is a constant, $D_B = D_B^*$

- \tilde{D} **Inter**-diffusion coefficient (or **chemical** diffusion coefficient)

One value for A-B binary substitutional alloy $\tilde{D} = D_A X_B + D_B X_A$

When $X_B \rightarrow 0$, $\tilde{D} = D_B = D_B^*$

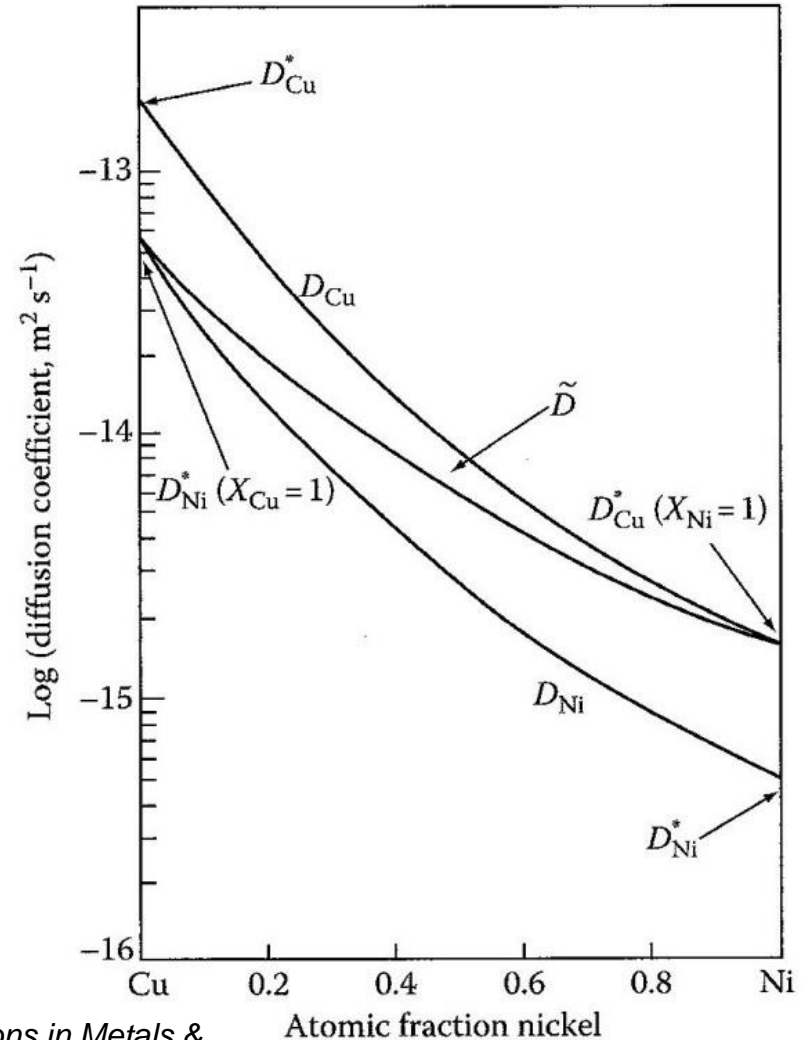


D_B^* vs. D_B vs. \tilde{D}

- ❑ Tracer diffusion coefficient D_B^* measured using radioactive elements in uniform pure element or alloy
- ❑ Inter-diffusion coefficient \tilde{D} determined via Boltzman-Manato method
- ❑ Intrinsic diffusion coefficient D_B determined from measured \tilde{D} and lattice velocity u via

$$\tilde{D} = D_A X_B + D_B X_A$$

$$u = (D_A - D_B) \frac{\partial X_A}{\partial x}$$



Phase Transformations in Metals & Alloys, Porter, 3rd Ed, 2008, p. 94