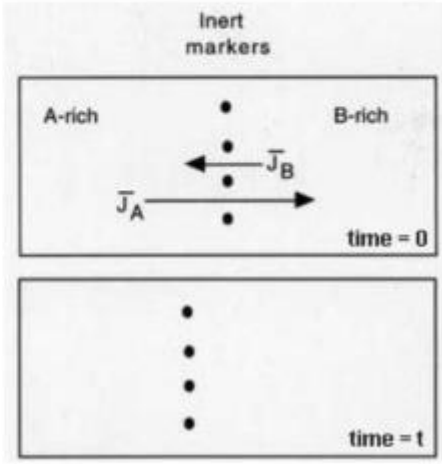
Chapter 5: Diffusion in Solids

Diffusion:	A process by which a matter is transported through another matter.

The *Kirkendall Effect*

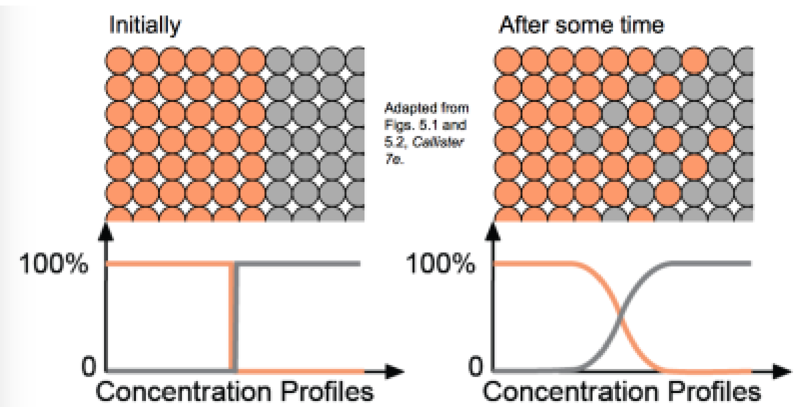
The *Kirkendall Effect*:	Describes what happens when two solids diffuse into each other at different rates.

- For a general case, *the Kirkendall Experiment* considers a diffusion couple A and B, where the diffusion rates of the two species are different.
  - $|J_A| > |J_B|$
- Since the diffusion fluxes are different, there will be a net flow of matter past the inert markers.
  - This causes the couple to shift bodily with respect to the markers.



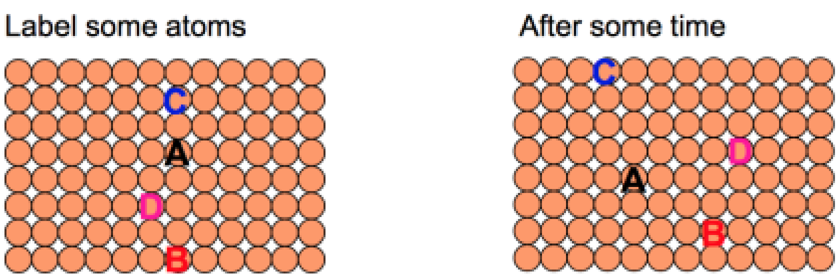
Diffusion

Inter-Diffusion:	In an alloy, atoms tend to migrate from regions of high concentration to regions of low concentration.
Self-Diffusion:	In an elemental solid, atoms also migrate.

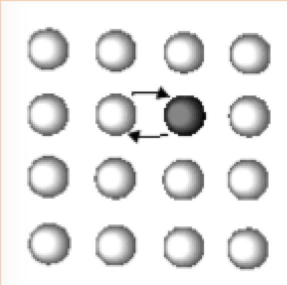
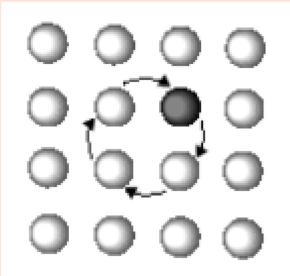


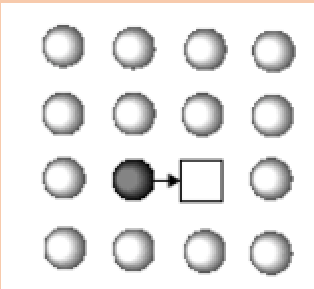
Inter-Diffusion

Self-Diffusion



How Does Diffusion Occur?

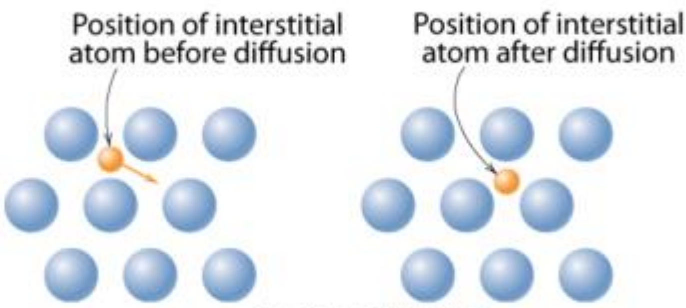
Direct Exchange Diffusion:		• This theory hypothesised that two atoms in a structure would switch positions with each other. • It was debunked, though, because the energy required to do this was too high.
Ring Mechanism:		• This theory hypothesised that atoms would all rotate position in a structure. • This theory required less energy to occur. • However, it was deemed improbable and debunked because it would require multiple atomic bonds to be broken.

Vacancy Mechanism:		• Theorised after the discovery of **vacancy defects**.
		• Atoms exchange their spot with a vacancy.
		• Requires far less energy to occur.
		• Applies to **substitutional impurity atoms**.
		• Rate depends on:
		    ○ Number of vacancies.
		    ○ Activation energy to exchange.
		• The current theory.

Interstitial Diffusion

Interstitial Diffusion:	Smaller atoms can diffuse between atoms. They move from one interstitial position to another interstitial position.

- Interstitial diffusion is faster than vacancy diffusion.
  - This is because there are more interstitial positions per atom than there are vacant positions per atom.
    - Therefore, higher probability of interstitial diffusion occurring.
  - The size of the interstitial atoms are also small, therefore, they require less energy to move.



Adapted from Fig. 5.3 (b), Callister 7e.

Processing Using Diffusion

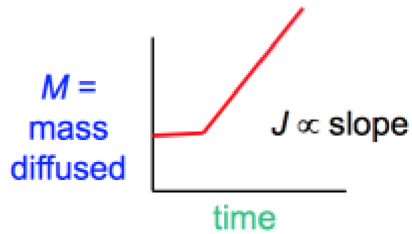
- **Case-Hardening** is a method of diffusing Carbon atoms into the host Iron atoms at the surface, in order to make it more resistant to wear.

How Do We Quantify the Amount or Rate of Diffusion?

$$J \equiv Flux \equiv \frac{moles\ (or\ mass) diffusing}{(Surface\ Area) \times (Time)} = \frac{mol}{cm^2 s}\ or\ \frac{kg}{m^2 s}$$

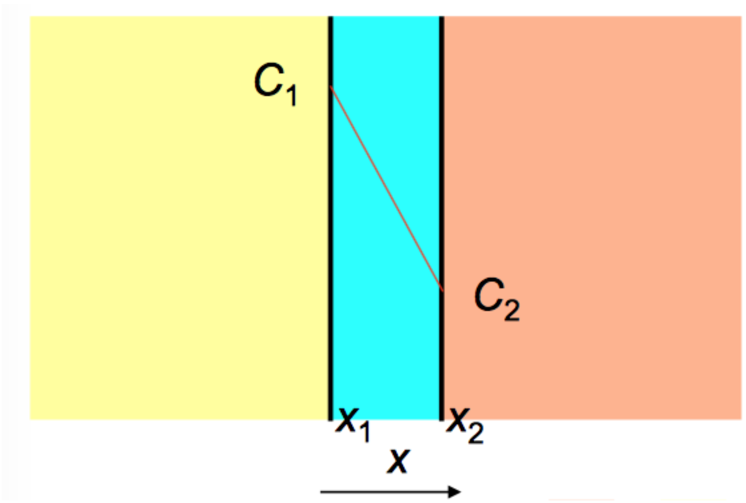
- Measured empirically:
  - Make the thin film (membrane) of known surface area.
  - Impose concentration gradient.
  - Measure how fast atoms or molecules diffuse through the membrane.

$$J = \frac{M}{At} = \frac{I}{A}\frac{dM}{dt}$$



Steady-State Diffusion

Steady-State Diffusion:	In steady-state diffusion, the Flux is constant with time – i.e. the rate of diffusion is independent of time.



- Flux is proportional to the concentration gradient = $\frac{dC}{dx}$.
- **Fick's First Law of Diffusion:**

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

D ≡ diffusion coefficient

- If it is linear:

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

Diffusivity

- Atoms will diffuse faster in an element with a BCC structure than in an element with a FCC structure.
  - This is because $APF_{BCC} = 0.68 < 0.74 = APF_{FCC}$
  - There is more free space in a BCC structure, therefore, it is easier to diffuse.
- Diffusivity depends upon:
  - **Type of Diffusion:** Whether the diffusion is interstitial or substitutional.
  - **Temperature:** As the temperature increases, diffusivity increases.
  - **Type of Crystal Structure:** BCC crystal has a lower APF than FCC, and hence, higher diffusivity.
  - **The Concentration of Diffusing Species:** Higher concentrations of diffusing solute atoms will affect diffusivity.