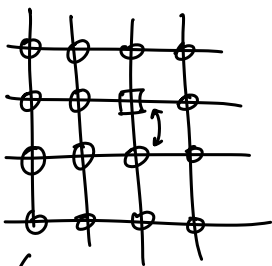


SUBSTITUTIONAL DIFFUSION:



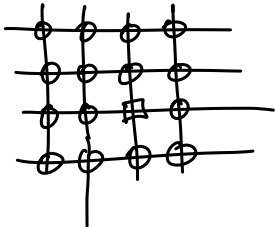
* Crystal defects play a key role in substitutional diffusion

↳ dislocations, grain boundaries, ...

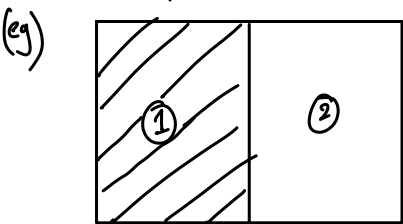
* Most common mechanism of mediating substitutional diffusion

⇒ VACANCY MECHANISM

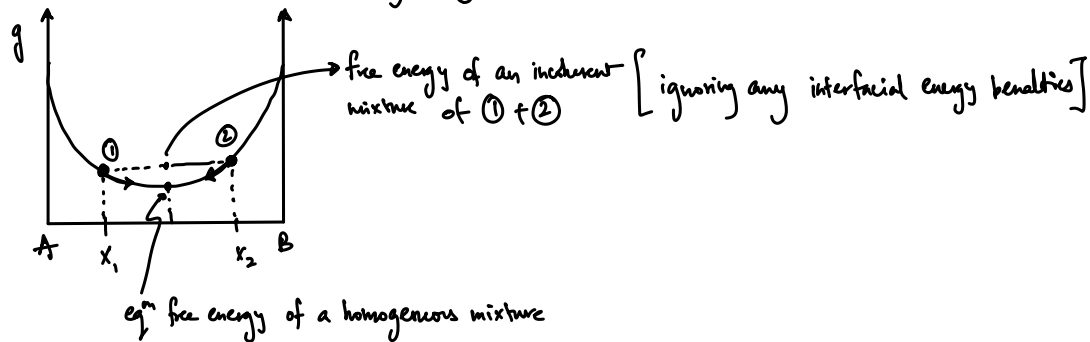
VACANCY SWAPS WITH A NEIGHBORING ATOM



Transport in substitutional solids requires sites & sources of vacancies ⇒ Can be generated from extended defects such as dislocations, grain boundaries, ...



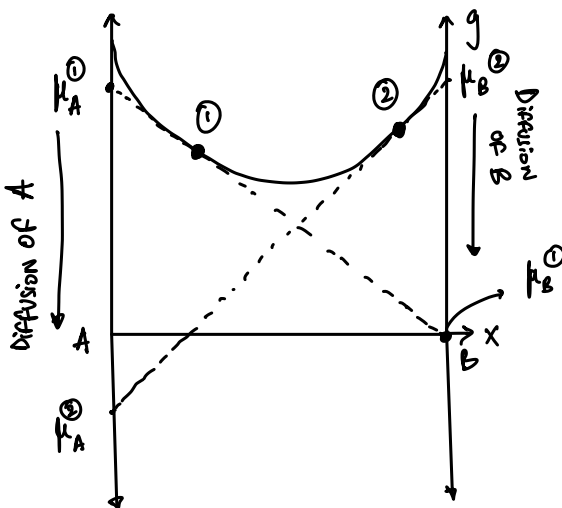
Weld two blocks of the same alloy having different concentrations



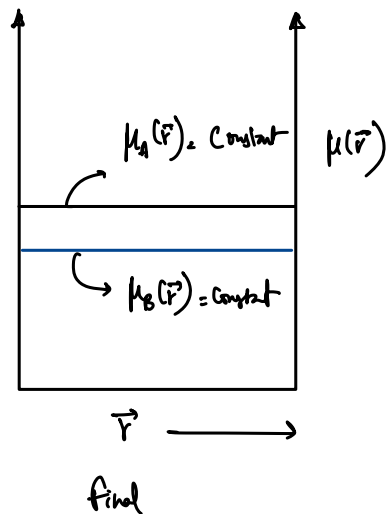
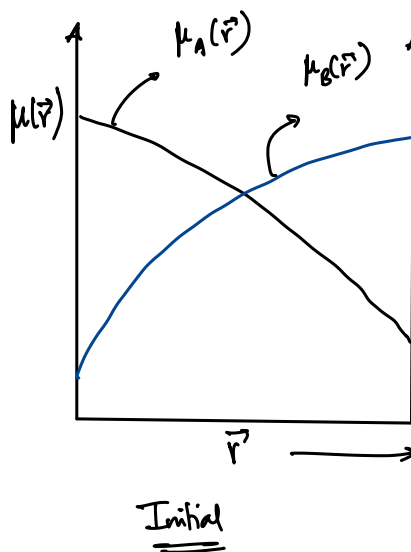
• A atoms diffuse from ① → ② (A-rich) (B-rich)

• B atoms go the other way

Diffusion & chemical potentials:



⇒ Diffusion occurs down chemical potential gradients.



* SUBSTITUTIONAL DIFFUSION IN A BINARY ALLOY:

3 species are involved in diffusion: A, B, V
 chemical elements vacancies.

The number of A & B atoms must be conserved

The number of vacancies are NOT conserved

- can be produced or annihilated at sources/sinks. (extended defects).

$$J_A(\nabla\mu_A, \nabla\mu_B, \nabla\mu_V), J_B, J_V$$

$$\left. \begin{aligned} J_A &= -L_{AA}\nabla\mu_A - L_{AB}\nabla\mu_B - L_{AV}\nabla\mu_V \\ J_B &= -L_{BA}\nabla\mu_A - L_{BB}\nabla\mu_B - L_{BV}\nabla\mu_V \\ J_V &= -L_{VA}\nabla\mu_A - L_{VB}\nabla\mu_B - L_{VV}\nabla\mu_V \end{aligned} \right\}$$

ONSALE RECIPROCALITY RELATIONS

$$\Rightarrow L_{AV} = L_{VA}, L_{AB} = L_{BA}, L_{BV} = L_{VB}$$

In a single crystal region:

$$J_A + J_B + J_V = 0 \Rightarrow \text{As the number of crystal sites are conserved } (X_A + X_B + X_V = 1)$$

$$\Rightarrow -(L_{AA} + L_{AB} + L_{AV})\nabla\mu_A - (L_{AB} + L_{BB} + L_{BV})\nabla\mu_B - (L_{AV} + L_{BV} + L_{VV})\nabla\mu_V = 0$$

the equation should hold for any set of chemical potential gradients.

$$\left[\begin{aligned} L_{AV} &= -(L_{AA} + L_{AB}) \\ L_{BV} &= -(L_{AB} + L_{BB}) \\ L_{VV} &= -(L_{AV} + L_{BV}) = L_{AA} + 2L_{AB} + L_{BB} \end{aligned} \right]$$

Using these relations with the linear flux equation.

$$J_A = -L_{AA}\nabla(\mu_A - \mu_V) - L_{AB}\nabla(\mu_B - \mu_V)$$

$$J_B = -L_{AB}\nabla(\mu_A - \mu_V) - L_{BB}\nabla(\mu_B - \mu_V)$$

In a solid with many sources/sinks for vacancies, \rightarrow vacancies will always be in eq^m locally.

\rightarrow eq^m criteria for vacancies $\Rightarrow \mu_V = 0$

$$\boxed{\begin{aligned} J_A &= -L_{AA}\nabla\mu_A - L_{AB}\nabla\mu_B \\ J_B &= -L_{AB}\nabla\mu_A - L_{BB}\nabla\mu_B \end{aligned}}$$

\rightarrow Looks identical to the flux equations we could have derived by ignoring vacancies, however there are important assumptions that must be kept in mind.

(Can we re-write these equations into a more recognizable form?)

$$J_B = -L_{AB}\nabla\mu_A - L_{BB}\nabla\mu_B$$

$$\text{Using Gibbs-Duhem: } X_A d\mu_A + X_B d\mu_B = 0 \Rightarrow \boxed{\nabla\mu_A = -\frac{X_B}{X_A}\nabla\mu_B}$$

$$J_B = +\frac{L_{AB}X_B}{X_A}\nabla\mu_B - L_{BB}\nabla\mu_B$$

$$J_B = - \left(\frac{L_{BB}}{x_B} - \frac{L_{AB}}{x_A} \right) x_B \nabla \mu_B$$

μ_B is a function of $x_B(\vec{r}) \Rightarrow \nabla \mu_B = \frac{\partial \mu_B}{\partial x_B} \nabla x_B$

$$J_B = - \underbrace{\left(\frac{L_{BB}}{x_B} - \frac{L_{AB}}{x_A} \right) x_B \frac{\partial \mu_B}{\partial x_B} \Omega}_{D} \nabla \left(\frac{x_B}{\Omega} \right)$$

\uparrow
 C_B

$\Omega \rightarrow$ volume / substitutional site
 Assume that the dependence on crystal concentration is negligible.

$$J_B = - D_B \nabla C_B$$

$D_B \rightarrow$ intrinsic diffusion coefficient

$$= \left(\frac{L_{BB}}{x_B} - \frac{L_{AB}}{x_A} \right) x_B \frac{\partial \mu_B}{\partial x_B} \Omega$$

$J_A = - D_A \nabla C_A \rightarrow$ same analysis as we did for B

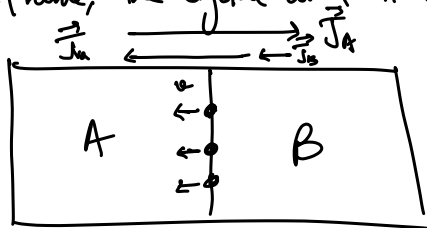
$J_B = - D_B \nabla C_B$

$J_{Va} = -(J_A + J_B)$

Notice that the Fickian fluxes only depend on gradients in concentration of the same specie.

* A FEW ADDITIONAL DETAILS:

- equations have been derived in the "crystal" frame of reference.
- In the lab reference frame, the crystal could move due to differences in diffusivities b/w A, & B



KIRKENDALL EFFECT.

The flux equations can be re-derived in the lab frame (see for example Chapter 3 of Kinetics of Materials)

$$\vec{J}_B = - \tilde{D} \frac{\partial C_B}{\partial r}$$

flux of B relative to the lab frame

$\tilde{D} = x_B D_A + x_A D_B =$ interdiffusion coefficient

- Assumes that Ω is independent of alloy composition
- x_i is independent of alloy composition