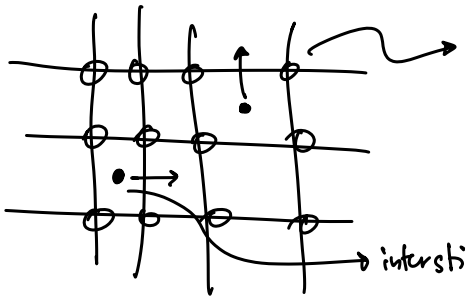
INTERSTITIAL DIFFUSION:



(say Fe or graphite) → forms a base crystal.

(say C @ Li)

interstitial atoms are usually much more mobile than "substitutional" atoms in the matrix phase.

1 → interstitial atom

2 → substitutional atom.

$$J_Q = -\frac{L_{QQ}}{T}\nabla T - L_{Q1}\nabla\mu_1 - L_{Q2}\nabla\mu_2$$

$$J_1 = -\frac{L_{1Q}}{T}\nabla T - L_{11}\nabla\mu_1 - L_{12}\nabla\mu_2$$

$$J_2 = -\frac{L_{2Q}}{T}\nabla T - L_{21}\nabla\mu_1 - L_{22}\nabla\mu_2$$

Simplify
- neglect temperature gradient
- Use the Gibbs-Duhem relationship:

$$\cancel{S dT} - \cancel{V dp} + N_1 d\mu_1 + N_2 d\mu_2 = 0$$

$$\Rightarrow N_1 \nabla\mu_1 = -N_2 \nabla\mu_2$$

$$\Rightarrow \nabla\mu_2 = -\frac{N_1}{N_2}\nabla\mu_1$$

X = composition of the interstitial specie / unit of substitution specie.

$$X = N_1/N_2$$

$$\boxed{\nabla\mu_2 = -X\nabla\mu_1}$$

- Substitutional atoms are very sluggish / do not move.

$$\boxed{J_2 = 0}$$

$$J_1 = -L_{11}\nabla\mu_1 + XL_{12}\nabla\mu_1$$

$$\boxed{J_1 = -(L_{11} - XL_{12})\nabla\mu_1}$$

@ $J = -L\nabla\mu$ for interstitial diffusion.

where "L" $= L_{11} - XL_{12}$

Let us simplify some more: $J = -L\nabla\mu$; $\nabla\mu = \left(\frac{\partial\mu}{\partial x}\right)\nabla x$

$$J = -L\left(\frac{\partial \mu}{\partial x}\right)\nabla x$$

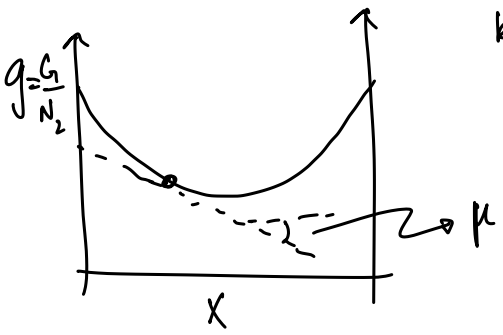
define: Ω = volume per substitutional site = $\frac{V}{N_2}$ (V: volume of the crystal; N_2: # of substitutional atoms.)

$$J = -L\Omega\left(\frac{\partial \mu}{\partial x}\right)\nabla\left(\frac{x}{\Omega}\right)$$

$$\frac{x}{\Omega} = \frac{N_1}{N_2 \times \frac{V}{N_2}} = \frac{N_1}{V} = C$$ (C: Concentration of interstial atom per unit volume.)

$$\boxed{J = -L\Omega\left(\frac{\partial \mu}{\partial x}\right)\nabla C} \quad \xleftrightarrow{\text{ficks 1st LAW}} \quad J = -D\nabla C$$

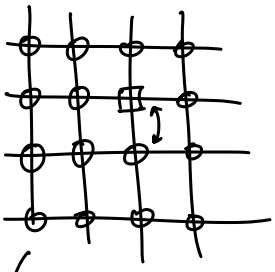
$$\boxed{D = L\Omega\left(\frac{\partial \mu}{\partial x}\right)}$$ ($\frac{\partial \mu}{\partial x}$: thermodynamic factor; L: kinetic factor)



$$\mu = \frac{\partial g}{\partial x} \Rightarrow \frac{\partial \mu}{\partial x} = \frac{\partial^2 g}{\partial x^2}$$

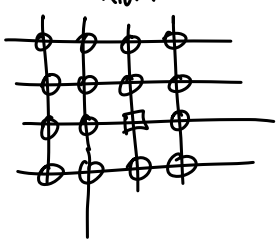
$$\boxed{D = L\Omega\frac{\partial^2 g}{\partial x^2}}$$

SUBSTITUTIONAL DIFFUSION:



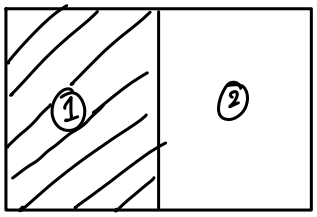
* Crystal defects play a key role in substitutional diffusion
  - → dislocations, grain boundaries, ...
* Most common mechanism of mediating substitutional diffusion
  - ⇒ VACANCY MECHANISM

VACANCY SWAPS WITH A NEIGHBORING ATOM

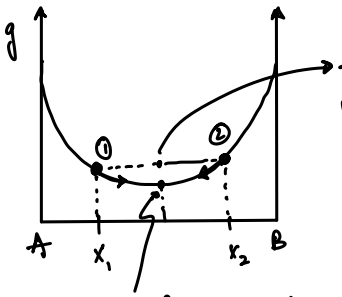


Transport in substitutional solids requires sinks & sources of vacancies ⇒ Can be generated from extended defects such as dislocations grain boundaries, ...

(eg)



Weld two blocks of the same alloy having different concentrations

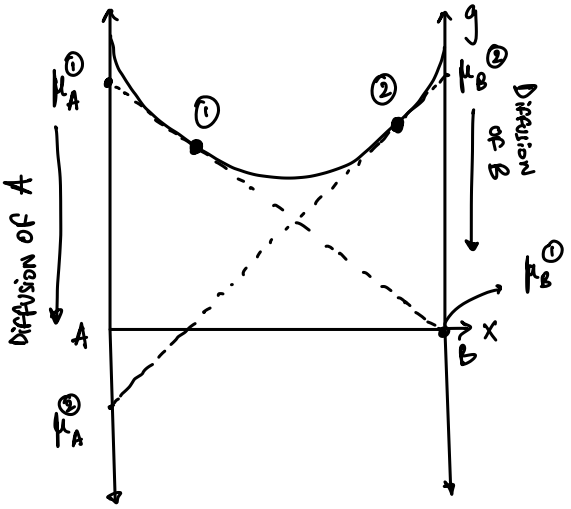


free energy of an inchoerent mixture of ① + ② [ignoring any interfacial energy penalties]

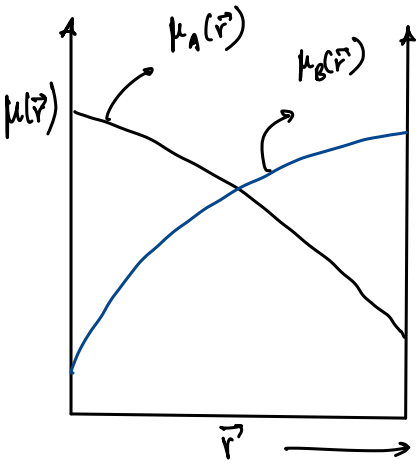
eqm free energy of a homogeneous mixture

- A atoms diffuse from ① → ② (A-rich) (B-rich)
- B atoms go the other way

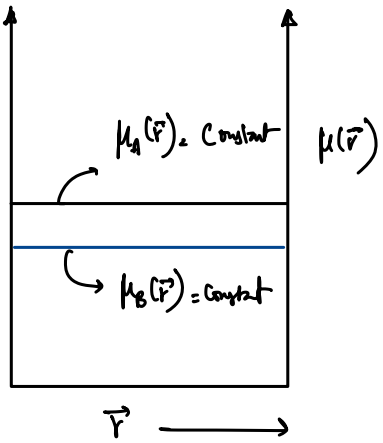
Diffusion & chemical potentials:



⇒ Diffusion occurs down chemical potential gradients.



Initial



final

* Substitutional Diffusion In A Binary Alloy:

3 Species are involved in diffusion: A, B (chemical elements), V (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).

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

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

Onsager Reciprocity Relations

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

In a single crystal region:

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

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

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

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

→ Using these relations with the linear flux equation.

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

In a solid with many sources/sinks for vacancies, → vacancies will always be in eqm locally.

→ eqm criteria for vacancies $\Rightarrow \mu_V = 0$

$$\left.\begin{aligned} J_A &= -L_{AA}\nabla\mu_A - L_{AB}\nabla\mu_B \\ J_B &= -L_{AB}\nabla\mu_A - L_{BB}\nabla\mu_B \end{aligned}\right]$$

→ 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?

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

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 $X_B(\vec{r}) \Rightarrow \nabla \mu_B = \frac{\partial \mu_B}{\partial X_B} \nabla X_B$

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

$\frac{X_B}{\Omega} = C_B$

$\Omega \longrightarrow$ Volume / Substitutional site

↳ Assume that the dependence on crystal concentration is negligible.

$$\boxed{J_B = -D_B \nabla C_B}$$

$D_B \longrightarrow$ intrinsic diffusion coefficient

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

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

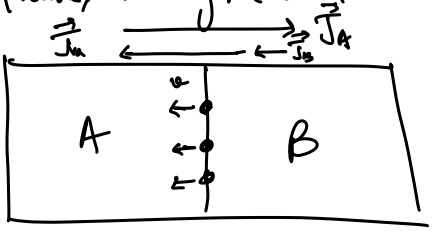
$J_B = -D_B \nabla C_B$

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

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)

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

$\tilde{J}_B$ ↳ 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_V is independent of alloy composition