The Diffusion Equation — I
Fick’s Laws of Diffusion

- Fick’s first law
  \[ \vec{J} = -D \nabla c \]
  The diffusivity, \( D \), is a second-rank tensor

- Fick’s second law
  \[ \frac{\partial c}{\partial t} = -\nabla \cdot \vec{J} \]
Self-diffusion

Self-diffusion in a chemically pure material

Involves diffusion of a radiotracer isotope that, while chemically identical to the host element, is easily tracked.

\[ J^C_{*1} = -kT \left[ \frac{L_{11}}{c_1} - \frac{L_{1*1}}{c_{*1}} \right] \cdot \frac{\partial c_{*1}}{\partial x} = -*D \cdot \frac{\partial c_{*1}}{\partial x} \]
Self-diffusion, cont’d

Self-diffusion in a homogeneous binary solution

Involves diffusion of a radiotracer isotope solute species that is easily tracked.

\[ J_{*1}^C = -kT \left[ \frac{L_{11}}{c_1} - \frac{L_{1*1}}{c_{*1}} \right] \cdot \frac{\partial c_{*1}}{\partial x} = -*D_1 \cdot \frac{\partial c_{*1}}{\partial x} \]
Vacancy mechanism of diffusion

- Self-diffusion in crystals, and diffusion of species in substitutional alloys, generally occurs by the *vacancy mechanism*.

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- Interdiffusion in an alloy with gradients of $c$

$$J^C_1 = -kT \left[ \frac{L_{11}}{c_1} - \frac{L_{12}}{c_2} \right] \left[ 1 + \frac{\partial \ln \gamma_1}{\partial \ln c_1} + \frac{\partial \ln \langle \Omega \rangle}{\partial \ln c_1} \right] \cdot \frac{\partial c_1}{\partial x} = -D_1 \cdot \frac{\partial c_1}{\partial x}$$

and

$$D_1 \equiv \left[ 1 + \frac{\partial \ln \gamma_1}{\partial \ln c_1} \right] \cdot *D_1 \text{ is the intrinsic diffusivity}$$
Interdiffusion

In a substitutional alloy of species 1 and 2, the self diffusivities $D_1$ and $D_2$ are generally different.

For the case illustrated, $D_1 > D_2$ and the species move at different rates. The flux difference is balanced by a net flow of vacancies from right to left.

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The Kirkendall effect

- Net flux of vacancies to the left makes inter-diffusion zone migrate toward the left in the figure.
- Inert particles placed at the interface of the diffusion couple move toward the left.
- Vacancies must be created on the right and migrate to the left of the interdiffusion zone where they are destroyed. Creation/destruction of vacancies is accomplished by dislocation climb.
Description of interdiffusion

- Interdiffusion is usually described in a volume-fixed reference frame, often called the laboratory frame, fixed relative to the specimen ends. In this frame,

\[
J_1^V = -[c_1 \Omega_1 D_2 + c_2 \Omega_2 D_1] \cdot \frac{\partial c_1}{\partial x} = \tilde{D} \cdot \frac{\partial c_1}{\partial x}
\]

\[
J_2^V = -[c_1 \Omega_1 D_2 + c_2 \Omega_2 D_1] \cdot \frac{\partial c_2}{\partial x} = \tilde{D} \cdot \frac{\partial c_2}{\partial x}
\]

and \( \tilde{D} = c_1 \Omega_1 D_2 + c_2 \Omega_2 D_1 \) is known as the interdiffusivity
Other driving forces for diffusion

We discussed above diffusion driven by gradients of chemical potential...more complex phenomena include:

- Diffusion of charged ions in ionic conductors
- Electromigration in metals
- Diffusion in a thermal gradient
- Capillarity-driven diffusion
- Stress-driven diffusion
Capillarity-driven diffusion

- Occurs as a result of the *Gibbs-Thomson* effect, which relates to the way chemical potentials differ in systems with curved interfaces, relative to systems with planar interfaces.

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Stress-driven diffusion

- Interstitials in a crystal are point centers of dilation and have associated stress fields that can interact strongly with other sources of inhomogeneous stress, e.g. dislocations.

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Stress-driven diffusion, cont’d

The diffusion potential $\Phi$ for an interstitial component 1 has an additional term proportional to the local hydrostatic stress $P$

$$\Phi_1 = \mu_1 + \Omega_1 P$$

and the diffusion equation takes the form

$$J_1 = -L_{11} \nabla (\mu_1 + \Omega_1 P) = -D_1 \left( \nabla c_1 + \frac{c_1 \Omega_1}{kT} \nabla P \right)$$