The Diffusion Equation — I

Fick's Laws of Diffusion

- Fick's first law

$$\vec{J} = -\mathbf{D}\nabla c$$

The diffusivity, **D**, is a second-rank tensor

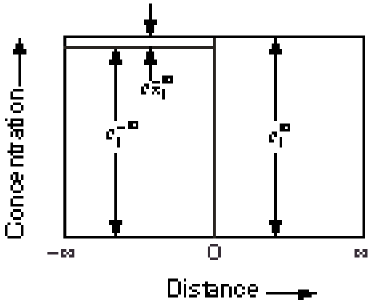
- Fick's second law

$$\frac{\partial c}{\partial t} = -\nabla \cdot \vec{J}$$

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.

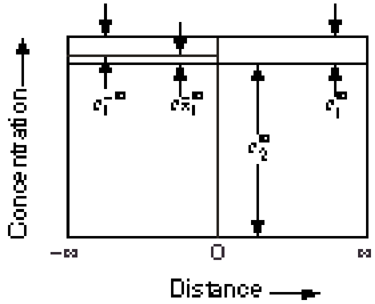


$$J_{*1}^{C} = -kT\left[\frac{L_{11}}{c_1} - \frac{L_{1*1}}{c_{*1}}\right]\cdot\frac{\partial c_{*1}}{\partial x} = -{}^{*}D\cdot\frac{\partial c_{*1}}{\partial x}$$

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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See Figure 8.2 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter.
Kinetics of Materials. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

- Interdiffusion in an alloy with gradients of *c*

$$J_1^C = -kT\left[\frac{L_{11}}{c_1} - \frac{L_{12}}{c_2}\right]\left[1 + \frac{\partial \ln \gamma_1}{\partial \ln c_1} + \frac{\partial \ln\langle\Omega\rangle}{\partial \ln c_1}\right] \cdot \frac{\partial c_1}{\partial x} = -D_1 \cdot \frac{\partial c_1}{\partial x}$$

and $D_1 \cong \left[1 + \frac{\partial \ln \gamma_1}{\partial \ln c_1}\right] \cdot {}^{*}D_1$ 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.

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See Figure 3.3 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter.
Kinetics of Materials. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

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.

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.

Figure removed due to copyright restrictions.
See Figure 3.7 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter.
Kinetics of Materials. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

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.

Figures removed due to copyright restrictions.
See Figures 3.8 and 3.9 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter.
Kinetics of Materials. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

Stress-driven diffusion, cont'd

- The diffusion potential Φ 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

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