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3.21 Kinetics of Materials—Spring 2006

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Lecture 3: Driving Forces and Fluxes for Diffusion. Self-Diffusion and Interdiffusion.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Section 3.1.
2. Poirier and Geiger, *Transport Phenomena in Materials Processing*, 1994, pp. 185–189 and 281–282 on heat conduction, and 417–434 on diffusion.

Key Concepts

- Fick's first law: $\vec{J} = -\mathbf{D}\nabla c$. This is an empirical law and it is consistent with the theory of linear irreversible thermodynamics.
- Fick's second law: $\frac{\partial c}{\partial t} = -\nabla \cdot \vec{J}$. This is a consequence of the conservation of matter. Note that if the diffusivity varies with c, the resulting differential equation is nonlinear.
- Self-diffusion in a chemically pure material can be measured by using a radioisotope that is easily tracked. The application of force-flux equations for the two isotopes yields a Fick's law-type expression for the radiotracer, KoM Eq. 3.4.
- Self-diffusion in a homogeneous alloy (uniform composition) can also be measured by using a radioisotope of one of the species. The application of force-flux equations for the various species present yields a Fick's law-type expression for the radiotracer, KoM Eq. 3.5.
- Self-diffusion in crystalline materials and in many alloy crystals occurs by the vacancy mechanism.
- Interdiffusion occurs in an alloy with composition gradients. The motion of each species in a laboratory frame fixed to the crystal follows Fick's first law, with a proportionality constant known as the *intrinsic diffusivity*. The intrinsic diffusivities and the self-diffusivities are related by KoM Eq. 3.13 and the relation involves a thermodynamic factor. Nonideality can either accelerate or retard interdiffusion kinetics, relative to kinetics measured in the absence of a chemical concentration gradient.
- Interdiffusion involves diffusion in a concentration gradient and the intrinsic diffusivities are not necessarily equal. This gives rise to a set of phenomena known as the *Kirkendall effect*. The interdiffusion can be described in a "volume-fixed" (laboratory) reference frame by a single diffusion coefficient known as the *interdiffusivity* which is related to the intrinsic diffusivities by the *Darken equation*, KoM Eq. 3.26.
- The equations of heat *conduction* are of identical form to Fick's laws: $\vec{J}_Q = -k\nabla T$ and $\frac{\partial T}{\partial t} = -\nabla \cdot \vec{J}_Q$

Simple Exercise

The diffusivity of boron in germanium obeys an Arrhenius law in the form $D = D_\circ \exp[-Q/(RT)]$, with $D_\circ = 5.1 \times 10^{-4}$ m^2 s^{-1} and $Q = 357$ kJ mol^{-1}. Calculate D at 800 C. At what temperature will the diffusivity be one order of magnitude smaller?