

3.205 Thermodynamics and Kinetics of Materials—Fall 2003

October 22, 2003

Kinetics Lecture 2: Heat conduction and mass diffusion

Lecture References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Chapter 3.
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.
- 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.
- 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. 3.12 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. 3.31.
- In addition to concentration gradients, other driving forces can lead to mass diffusion. These include thermal gradients, stress gradients, and capillary driving forces.
- The equations of heat *conduction* are of identical form to Fick's laws: $\vec{J}_Q = -k\nabla T$ and $\frac{\partial T}{\partial t} = -\nabla \cdot \vec{J}_Q$

Example Problem 03

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