

3.21 Kinetics of Materials—Spring 2006

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Lecture 13: Atomic Models for Diffusivities.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Section 8.2.
2. Allen and Thomas, *The Structure of Materials*, Section 5.1.6, “Point Imperfections in Ionic Crystals.”

Key Concepts

- The relation $D = \Gamma r^2 \mathbf{f} / 6$ can be applied to various diffusion processes and the resulting expressions enable a more complete understanding of the dependence of D on temperature and other factors.
- The diffusivity of solute atoms by interstitial jumps in the b.c.c. structure is uncorrelated and the resulting expression for D takes the form $D_I = (a^2/6)\nu \exp(S^m/K) \exp[-H^m/(kT)]$.
- The vacancy diffusivity in the f.c.c. structure is uncorrelated and when the vacancies make nearest-neighbor jumps the expression for D takes the form $D_V = a^2\nu \exp(S_V^m/K) \exp[-H_V^m/(kT)]$.
- The self-diffusivity of a tracer atom in the f.c.c. structure by the vacancy mechanism involves jumps that can only occur when the tracer exchanges places with a neighboring vacancy. Thus, the vacancy concentration which at equilibrium is given by $X_V = \exp(S_V^f/K) \exp[-H_V^f/(kT)]$ must enter the desired expression for *D . In addition, while the vacancy jumps will be uncorrelated, the tracer atom jumps will be correlated so the resulting expression for *D takes the form $^*D = \mathbf{f} a^2\nu \exp[(S_V^m + S_V^f)/K] \exp[-(H_V^m + H_V^f)/(kT)]$. Detailed analysis of the correlated jumping of the tracer atoms leads to the approximate expression $\mathbf{f} \approx (z - 1)/(z + 1)$, where z is the coordination number for the crystal structure in which the tracers are jumping. A more complete analysis indicates that $\mathbf{f} \approx 0.78$ in f.c.c. crystals.
- The expressions for D written above all obey an *Arrhenius law* of the form $D = D^\circ \exp[-E/(kT)]$. Depending on the mechanism of diffusion, the *activation energy* E may have contributions from both defect *migration* and *formation* processes.
- The *isotope effect* refers to the small effect of mass of the diffusing species on diffusivity in tracer diffusion processes. For species of masses m_1 and m_2 , $^*D_1/^*D_2 = \sqrt{m_2/m_1}$.
- Complexities of solute-atom diffusion by the vacancy mechanism in binary alloys can be appreciated with the *three-frequency model* for jumping, in which the vacancy jump rates may differ depending on whether the exchange is with the solute atom, a near-neighbor to the solute atom, or a more distant neighbor to the solute atom.

Related Exercises in *Kinetics of Materials*

Review Exercises 8.12–8.15, pp. 199–201.