

3.21 Kinetics of Materials—Spring 2006

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Lecture 14: Atomic Models for Diffusivities—II.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Section 8.2.

Key Concepts

- Point defects in ionic crystals generally have an associated local charge. A unit cell in a perfect crystal has zero net charge. The charge associated with a point defect is equal to the net charge in a unit cell containing the defect. Thus, a cation vacancy (a vacancy on site normally occupied by a cation) has a net *negative* charge, and an anion interstitial has a net *positive* charge. The *Kröger-Vink notation* is used to specify the type of imperfection, its site in the crystal, and its effective charge.
- Normally ionic crystals are charge-neutral and thus the populations of positively charged defects is constrained by that of negatively charged defects.
- *Intrinsic defects* in ionic crystals include anion and cation defects associated with the pure material. A *Frenkel defect* consists of nearby vacancy-interstitial pairs, e.g. in LiF a cation Frenkel defect would consist of V_{Li}^{\prime} and Li_i^{\bullet} . A *Schottky defect* consists of nearby charge-compensating anion vacancy-cation vacancy pairs, e.g. in ZrO_2 a Schottky defect would consist of V_{Zr}^{\prime} and *two* $V_O^{\prime\prime}$.
- *Extrinsic defects* in ionic materials arise from impurity ions and may be accommodated interstitially or substitutionally as dictated by their relative energies. *Isovalent* ions are generally accommodated substitutionally and have zero net charge. *Aliovalent* ions may be accommodated either substitutionally or interstitially depending on ion size, charge, and other considerations. Introduction of aliovalent impurities into an ionic crystal often leads to the formation of additional charge-compensating defects such as vacancies.
- Equilibrium concentrations of point defects in ionic crystals may be calculated by knowing values for equilibrium constants for formation of intrinsic defects as well as by accounting for the constraints imposed by charge neutrality. When impurities are present a material might have mainly intrinsic defect populations at high temperatures, and defects dominated by extrinsic defects associated with impurities at low temperatures (see *KoM* pp. 179–180).
- The diffusivities in ionic crystals can be modeled using the relation $D = \Gamma r^2 f / 6$ using analogous methods to those for metallic materials. In impure ionic crystals, this can lead to changes in activation energies for diffusion depending on whether the point defects involved in the diffusion are in the intrinsic or extrinsic regime (see *KoM* Fig. 8.13).
- When cations can exist in multiple oxidation states (e.g., in transition metals), ionic materials may have defects that lead to *nonstoichiometry* and associated point and electronic (i.e., electrons and holes) defects. In nonstoichiometric oxides this can lead to regimes in which the cation diffusivity can be *oxygen partial-pressure dependent* (see *KoM* Fig. 8.15).

Related Exercises in *Kinetics of Materials*

Review Exercises 8.15–8.19, pp. 201–205.