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3.205 Thermodynamics and Kinetics of Materials—Fall 2006

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Kinetics Lecture 5: Mechanisms of Diffusion—II. Ionic Crystals.

Lecture References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Section 8.2.2, "Ionic Solids," pp. 177–182.
2. Allen and Thomas, *The Structure of Materials*, John Wiley & Sons, New York, 1999. Section 5.1.6, "Point Imperfections in Ionic Crystals," pp. 263–270 contains a good introduction to Kröger-Vink notation, Schottky and Frenkel defects, and impurity-ion incorporation.
3. Chiang, Birnie, and Kingery, *Physical Ceramics*, John Wiley & Sons, New York, 1997. Sections 2.1, "Point Defects," 3.2, "Atomistic Diffusion Processes," and 3.3, "Electrical Conductivity" are all relevant. Also, see information on oxygen sensors on pp. 142–146 and 234–235.

Key Concepts

- Point imperfections in ionic crystals generally have associated net charges.
- The positive ions are called *cations* and the negative ions are *anions*. The anions are generally significantly larger than the cations.
- The Kröger-Vink notation is used to specify point imperfections in ionic crystals.
- There are two types of *intrinsic* point defects in ionic crystals: *Schottky defects* and *Frenkel defects*. Schottky defects consist of charge-compensating anion and cation vacancies. Frenkel defects consist of vacancy-interstitial pairs.
- *Extrinsic* defects in ionic crystals arise when impurity species are present. *Isovalent* impurities have the same charge as one of the ions in the pure crystal and substitute for that ion. *Aliovalent* impurities have a different charge than the ion for which they substitute, and they lead to charge-compensating point defect formation that can influence diffusion behavior, particularly at low temperatures.
- Diffusion in the intrinsic regime involves motion of the ions by migration of intrinsic defects. In the extrinsic regime, point defects involved in diffusion arise from the impurities that are present and the impurity concentration controls the point defect concentration and hence has a strong role on determining the diffusivities.
- Ionic crystals may also contain *electronic* defects such as localized electrons and holes. These are found in nonstoichiometric transition-metal oxides, and because their concentration typically is oxygen partial-pressure dependent, such materials can be used as chemical sensors.

Example Problem

Consider the incorporation of magnesia, MgO, into alumina, $\mathrm{Al_2O_3}$, to form a solid solution. Write two defect incorporation reactions using Kröger-Vink notation, one assuming that the Mg^{2+} cations substitute for Al^{3+} and the second assuming the formation of some cation interstitials. Ensure that your reactions have charge, mass, and site balance.