

## Topic 3: how do point defects react in an open system?

### Overview

In many solid systems, point defects are responsible for interactions with the outside environment; while it was only in the last century that we realized diffusion was even possible in solids, it is now known to be fundamental to how materials can vary from stoichiometry, and maintain equilibrium in contact with other materials or even gases. Not surprisingly, temperature plays an important role in both thermodynamic equilibrium as well as kinetics.

Making all of these matters even more interesting, the same defects respond both to changes in chemical potentials *and* electrostatic potentials, as charge neutrality is maintained inside the material: free electrons requires compensating positive defects (which might not be holes!), and free holes requires compensating negative defects (which might not be electrons!).

### Reading

For this topic, you will want to read some of review articles about stabilized zirconia ( $\text{ZrO}_2$ ). It is possible to stabilize the cubic structure of zirconia by adding different dopants, one of the most familiar being yttria ( $\text{Y}_2\text{O}_3$ ), but others are possible. The papers below discuss defects and stabilization, while the last two discuss specific reactions at an interface.

- P. Li, I.-W. Chen, and J. E. Penner-Hahn, “Effect of Dopants on Zirconia Stabilization—An X-ray Absorption Study: I, Trivalent Dopants.” *J. Am. Ceram. Soc.* **77**, 118-128 (1994): doi:10.1111/j.1151-2916.1994.tb06964.x
- S. Fabris, A. T. Paxton, M. W. Finnis, “A stabilization mechanism of zirconia based on oxygen vacancies only.” *Acta Mater.* **50**, 5171-5178 (2002): doi:10.1016/S1359-6454(02)00385-3
- T. Wagner, R. Kirchheim, M. Rühle, “Electrochemically-induced reactions at Ni/ $\text{ZrO}_2$  interfaces.” *Acta Metall. Mater.* **40** S85-S93, (1992): doi:10.1016/0956-7151(92)90267-I
- T. Wagner, R. Kirchheim, M. Rühle, “Chemical reactions at metal/ceramic interfaces during diffusion bonding.” *Acta Metall. Mater.* **43** 1053-1063 (1995): [http://dx.doi.org/10.1016/0956-7151\(94\)00297-U](http://dx.doi.org/10.1016/0956-7151(94)00297-U)

### Team assignment

Considering the work of Wagner *et al.* on diffusion bonding, your team is interested in the influence of temperature. Their experiments were performed at  $1000^\circ\text{C}$ ; you plan to perform similar experiments, but over a range of temperatures.

1. What changes would you expect if the temperature were raised?
2. What changes would you expect if the temperature were lowered?
3. You want to publish groundbreaking research that will get you job offers before you’ve even outlined your dissertation, so: What temperature range do you think would be interesting?

### Prelecture questions

1. Schottky defects are dominant in a crystal of NaCl. A law of mass action describes the neutral concentrations  $[\text{V}_{\text{Na}}^\times][\text{V}_{\text{Cl}}^\times] = A \exp[-\Delta G_0/k_B T]$ . Assume that the vacancies ionize.

- The impurity  $\text{CdCl}_2$  is dissolved into  $\text{NaCl}$  to a concentration of  $[\text{Cd}]$ . How does the total concentration of cation vacancies  $[\text{V}_{\text{Na}}]$  vary vs.  $1/T$ ?
2. Consider  $\text{ZrO}_2$  without any dopants, and assume that the dominant defects are oxygen vacancies, zirconium interstitials, electrons and holes. We want to understand how defect concentrations would be affected by the partial pressure of oxygen gas to which zirconia is exposed. What defect reactions are important to consider? Make sure to include ionization reactions for point defects.
  3. Using your reactions from the previous question, estimate how the conductivity of zirconia varies with oxygen gas partial pressure in the limit of low partial pressure. Assume that oxygen vacancies have a lower formation energy than zirconium interstitials.

### Suggested background

These may help you think about the papers and questions raised; you may want to look beyond these, too.

- Joachim Maier, *Physical Chemistry of Ionic Materials: Ions and Electrons in Solids*. Chapter 5: doi:10.1002/0470020229
- Manfred Martin, “Diffusion in Oxides” (sections 5.1-5.2) from *Diffusion in Condensed Matter: Methods, Materials, Models*. (Springer) doi:10.1007/3-540-30970-5\_5
- Course webnotes:
  - 2.1.2 Frenkel defects, 2.1.3 Schottky defects, 2.1.4 Mixed point defects
  - 2.4.1 Motivation and basics, 2.4.2 Kröger-Vink notation, 2.4.3 Schottky notation
  - 2.4.4 Brouwer diagram
- Slides (on Google Drive):
  - Ionic Defects
  - Electroneutrality
  - Open System Defect Reactions

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Discussion: Sept. 24-26, 2024