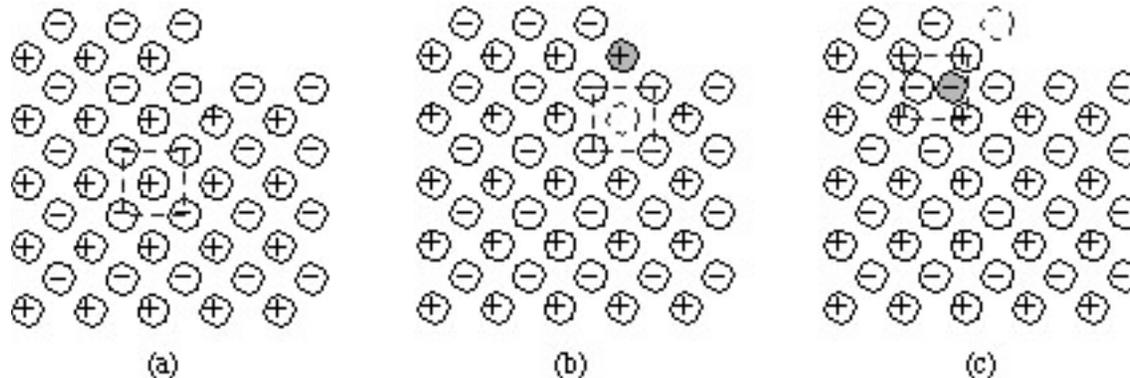


Mechanisms of Diffusion—II. Ionic Crystals

Charges on point imperfections

- Point imperfections in ionic crystals are generally electrically charged.



- (a) Unit cell in perfect crystal; charge-neutral.
(b) Removal of a cation to a surface step, leaving a unit cell with a cation vacancy. Net charge associated with defective cell is -1 . (c) Formation of anion interstitial; net charge is -1 .



Kröger-Vink notation

$$X_Y^Z \text{ where } \begin{cases} X = \text{what is at the site (El or V)} \\ Y = \text{what site is defective (El or } i) \\ Z = \text{effective charge at the site } (\bullet = +; ' = -) \end{cases}$$

■ Examples

Intrinsic defects: Schottky and Frenkel

Defects involving impurities

Schottky disorder

- Charge-compensating anion vacancies + cation vacancies — e.g. in MgO

Formation: $\text{null} = V_{\text{Mg}}'' + V_{\text{O}}^{\bullet\bullet}$

Equilibrium: $K_S = [V_{\text{Mg}}''] \cdot [V_{\text{O}}^{\bullet\bullet}] = \exp\left(-\frac{G_S^f}{kT}\right)$

Charge neutrality: $[V_{\text{Mg}}''] = [V_{\text{O}}^{\bullet\bullet}]$

Frenkel pair

- Charge-compensating vacancy-interstitial pair — e.g. cation Frenkel pair in LiF



Equilibrium: $K_F = [V'_{\text{Li}}] \cdot [\text{Li}_i^{\bullet}] = \exp\left(-\frac{G_F^f}{kT}\right)$

Charge neutrality: $[V'_{\text{Li}}] = [\text{Li}_i^{\bullet}]$

Self-diffusion in KCl

- Analogous to self-diffusion in metals with

$$[V'_K] = \exp\left(-\frac{G_S^f}{2kT}\right) = \exp\left(\frac{S_S^f}{2k}\right) \cdot \exp\left(-\frac{H_S^f}{2kT}\right)$$

and

$$\Gamma_K = 12\Gamma'_K[V'_K]$$

giving for the self-diffusivity on the cation sites

$$D^K = ga^2 f\nu \exp\left(\frac{S_{CV}^m + S_S^f/2}{k}\right) \cdot \exp\left(-\frac{H_{CV}^m + H_S^f/2}{kT}\right)$$

Extrinsic defects

- Isovalent impurities — e.g. CaO in MgO



- Equilibrium:
$$K_S = [V_{\text{Mg}}''] \cdot [V_{\text{O}}^{\bullet\bullet}] = \exp\left(-\frac{G_S^f}{kT}\right)$$

- Charge neutrality:
$$[V_{\text{Mg}}''] = [V_{\text{O}}^{\bullet\bullet}]$$

- Impurity does not influence point defect concentration

Extrinsic defects, cont'd

- Aliovalent impurities — e.g. CaO in ZrO₂



- Equilibrium: $K_S = [\text{V}_{\text{Zr}}^{4-}] \cdot [\text{V}_{\text{O}}^{\bullet\bullet}]^2 = \exp\left(-\frac{G_S^f}{kT}\right)$

- Charge neutrality: $4[\text{V}_{\text{Zr}}^{4-}] + 2[\text{Ca}_{\text{Zr}}''] = 2[\text{V}_{\text{O}}^{\bullet\bullet}]$

- Impurities influence point defect concentration

Cation diffusion in KCl with Ca

- Impurity incorporation



Schottky equilibrium

$$K_S = [\text{V}_{\text{K}}'] \cdot [\text{V}_{\text{Cl}}^{\bullet}] = \exp\left(-\frac{G_S^f}{kT}\right)$$

Neutrality condition

$$[\text{V}_{\text{Cl}}^{\bullet}] + [\text{Ca}_{\text{K}}^{\bullet}] = [\text{V}_{\text{K}}']$$

Diffusion in KCl with Ca, cont'd

- This leads to

$$[V'_K] = \frac{[Ca_{\dot{K}}]}{2} \cdot \left[1 + \left\{ 1 + \frac{4[V'_K]_{\text{pure}}^2}{[Ca_{\dot{K}}]^2} \right\}^{1/2} \right]$$

and to two regimes:

Intrinsic: Small impurity concentration or high T

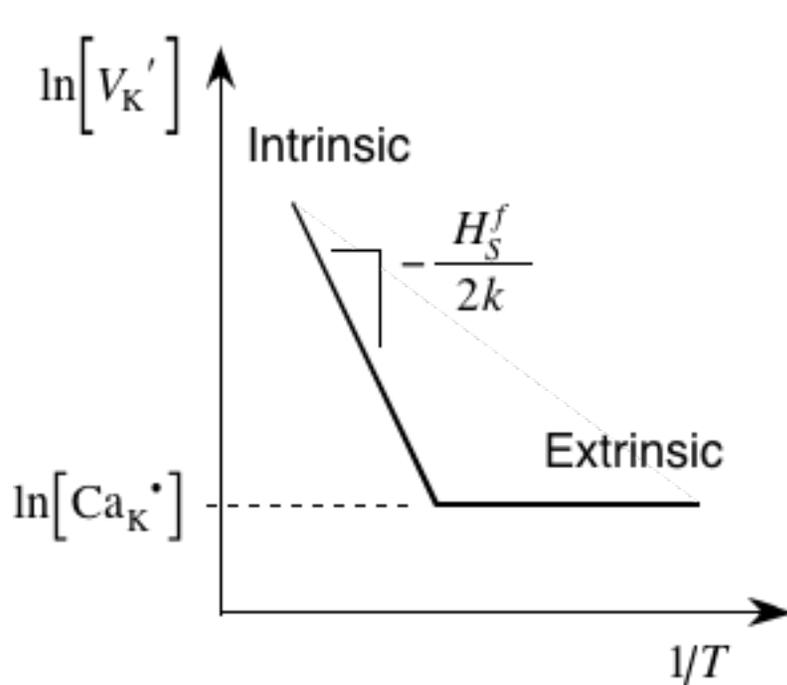
$$[V'_K]_{\text{pure}} \gg [Ca_{\dot{K}}], \text{ then } [V'_K] = [V'_K]_{\text{pure}}$$

Extrinsic: High impurity concentration or low T

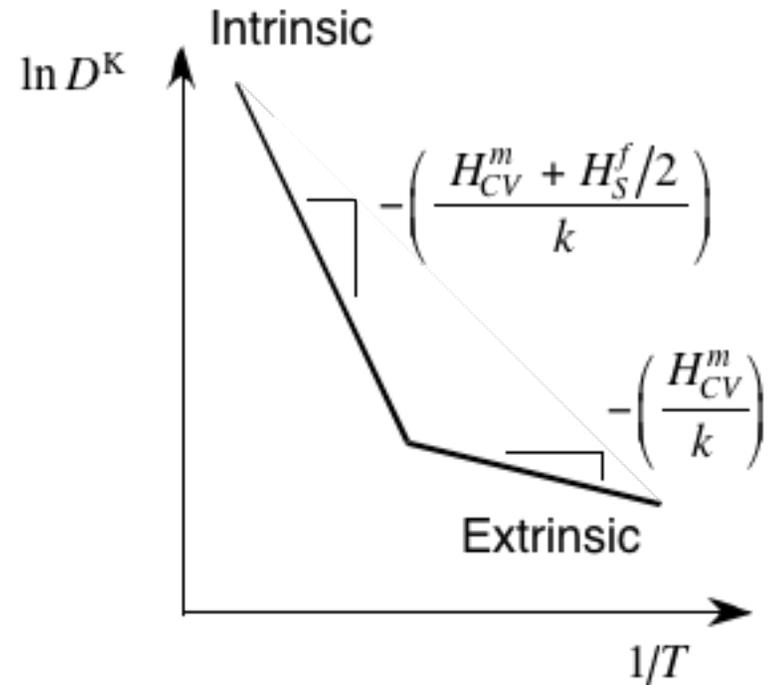
$$[V'_K]_{\text{pure}} \ll [Ca_{\dot{K}}], \text{ then } [V'_K] = [Ca_{\dot{K}}]$$

Diffusion in KCl with Ca, cont'd

- This leads to this behavior for the cation diffusivity



Cation vacancy concentration

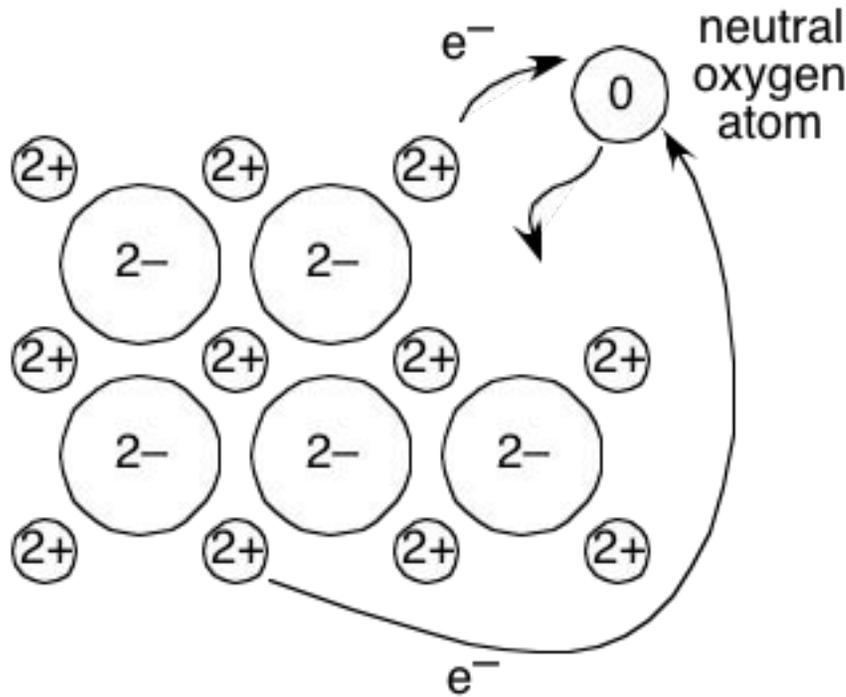


Cation diffusivity

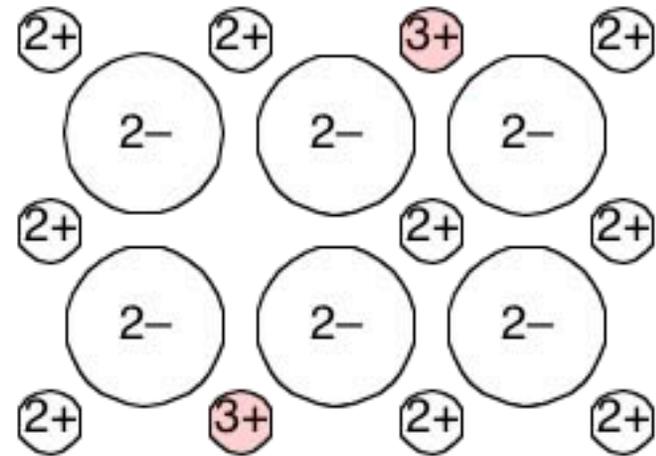
• Diffusion In nonstoichiometric oxides

– e.g., cation diffusion in FeO (note various valence states of Fe are possible)

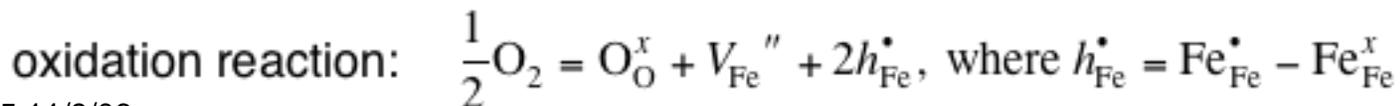
FeO can be oxidized to make a cation deficient oxide $Fe_{1-x}O$



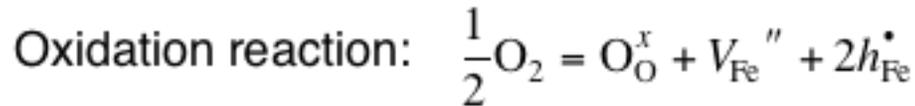
Oxygen atom approaches, attracts two electrons from Fe^{2+} and gets ionized.



Oxygen-deficient crystal. Note cation vacancy and two ferric cations.



• Diffusion in nonstoichiometric FeO, cont'd:



Equilibrium constant for this reaction: $K_{eq} = \frac{[V_{Fe}''] \cdot [h_{Fe}^\bullet]^2}{\sqrt{p_{O_2}}} = \exp\left(-\frac{\Delta G}{kT}\right)$

Charge neutrality: $2[V_{Fe}''] = [h_{Fe}^\bullet]$

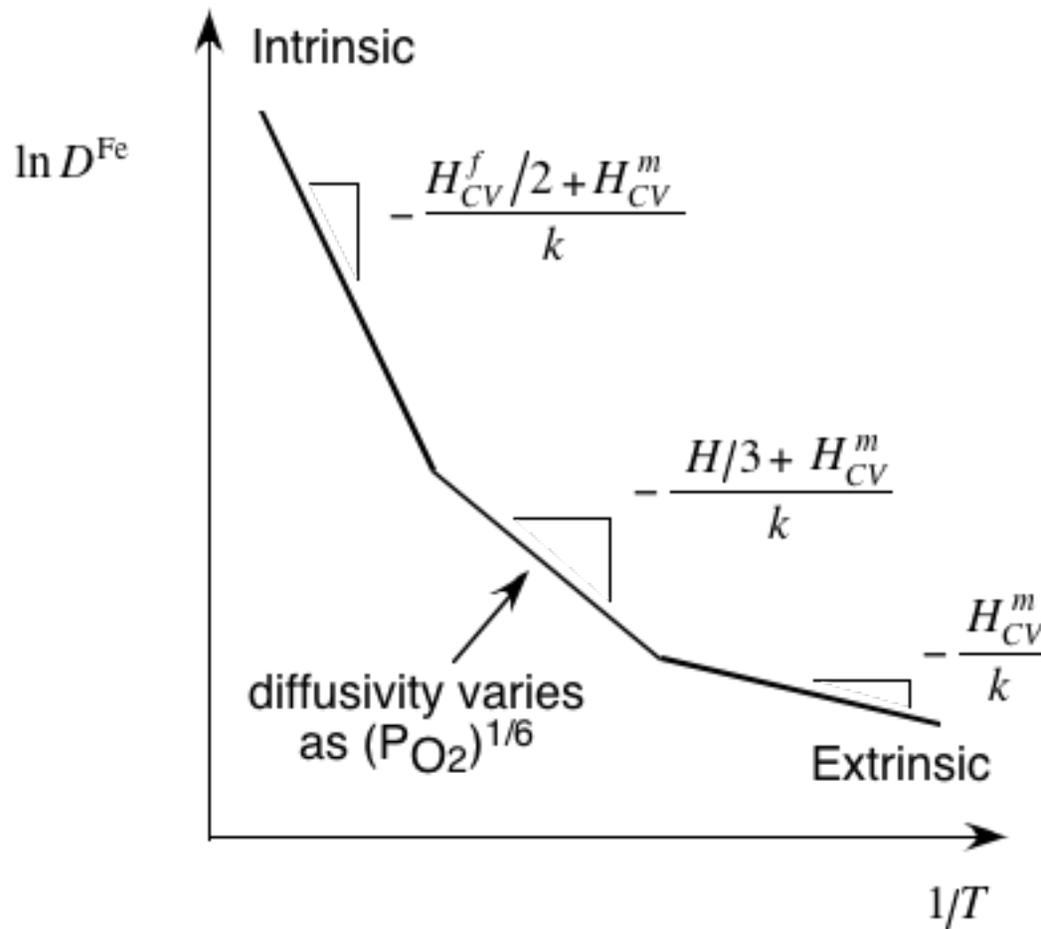
Cation vacancy concentration: $[V_{Fe}''] = (1/4)^{1/3} \exp\left(-\frac{\Delta G}{3kT}\right) (p_{O_2})^{1/6}$

Diffusion in impure FeO will have *three* regimes:

1. High T , low oxygen pressure, dominated by Schottky defect equilibria
2. High oxygen pressure, dominated by oxidation reaction
3. Low T , low oxygen pressure, dominated by extrinsic impurities

• Diffusion In nonstoichiometric FeO, cont'd:

Cation diffusivity Arrhenius plot



Position of middle segment will depend on oxygen pressure, hence this region will not be observable at low oxygen pressures or high impurity contents

• Diffusion in ceramics: relevance

Microstructural processes

Densification of powder compacts by sintering

Creep deformation at high temperatures

Grain growth

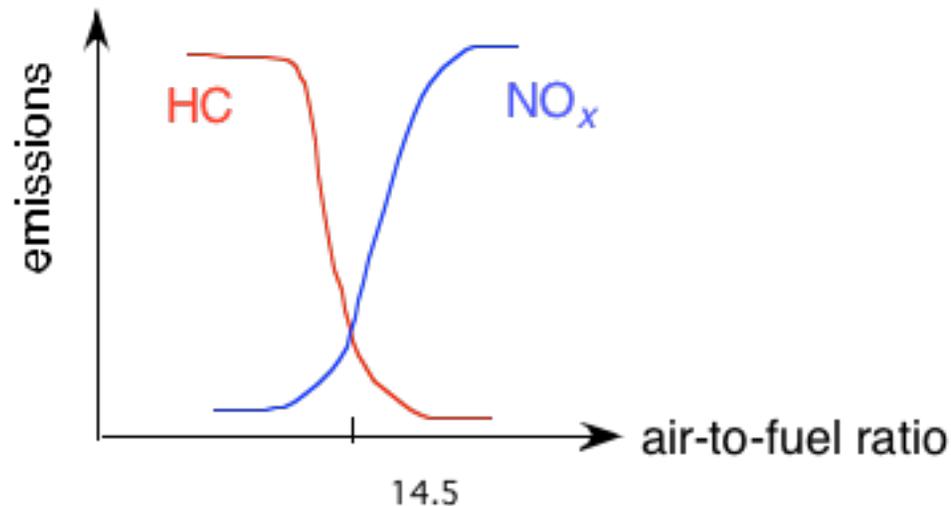
Solid–solid transformation kinetics, including oxidation of metals

Electrical conduction

Ionic conductors for chemical and gas sensors, solid electrolytes, fuel cells

Sensors

**The automotive
oxygen sensor**





The automotive oxygen sensor, cont'd:

TiO₂-based, works on *electronic* conduction that has pO₂ dependence

**ZrO₂-Y₂O₃-based, works on electrochemical potential difference between
exhaust stream and ambient air**

References for additional study:

Chiang et al., *Physical Ceramics*, 1997.

Section 2.1 on Point Defects

Section 3.2 on Atomistic Diffusion Processes

Section 3.3. on Electrical Conductivity

Oxygen sensors, pp. 142–146 and pp. 234–235