Previous lecture

• Diffusion mechanisms in crystals: vacancy, interstitial, intersticialcy

• Expressions for D:

Diffusivity of interstitial solute in bcc crystal

$$D = \frac{a^2}{6} \ \exp\left(s^m/k \right) \exp\left(- h^m/kT \right) \qquad f = 1$$

Self diffusion by vacancy mechanism

$$D = f\, a^2 \ \exp \ \frac{s_v^{\,m} + \ s_v^{\,f}}{k} \ \exp \ -\frac{h_v^{\,m} + \ h_v^{\,f}}{kT} \qquad f \quad 1 - \frac{2}{z}$$

Solute diffusion by vacancy mechanism: three-frequency model

• Background on defects in ionic crystals and Kröger-Vink notation

Today

• Atomistic models for diffusion coefficients - ionic crystals

Intrinsic and extrinsic regimes in stoichiometric material

• Diffusion in nonstoichiometric oxides; the oxygen sensor

• Role of microstructure in diffusion: short-circuiting   KPIM Chapter 9

- **Cation diffusion in KCl with Ca impurities**

Impurity incorporation $CaCl_2 \xrightarrow{KCl} Ca_K^{\bullet} + 2Cl_{Cl}^x + V_K'$

Schottky equilibrium $K_S = \left[V_K'\right]\left[V_{Cl}^{\bullet}\right] = \exp\left(-\dfrac{g_S^f}{kT}\right)$

Neutrality condition $\left[V_K'\right] = \left[V_{Cl}^{\bullet}\right] + \left[Ca_K^{\bullet}\right]$

So we have $\left[V_K'\right] = \dfrac{\left[Ca_K^{\bullet}\right]}{2}\left(1 + \sqrt{1 + \dfrac{4K_S}{\left[Ca_K^{\bullet}\right]^2}}\right)$

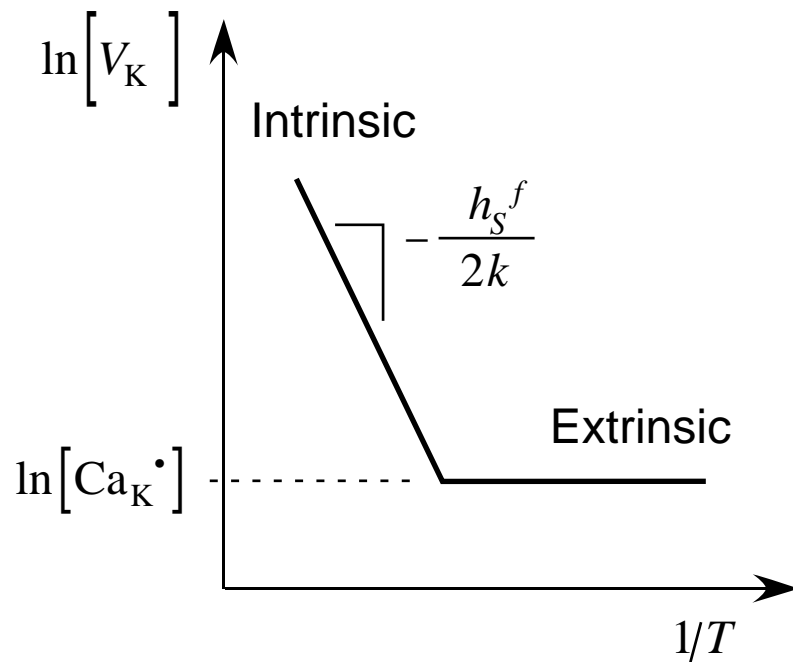*Intrinsic regime*: impurity concentration is small or *T* is high and thus

$$\left[V_K'\right] = \sqrt{K_S}$$

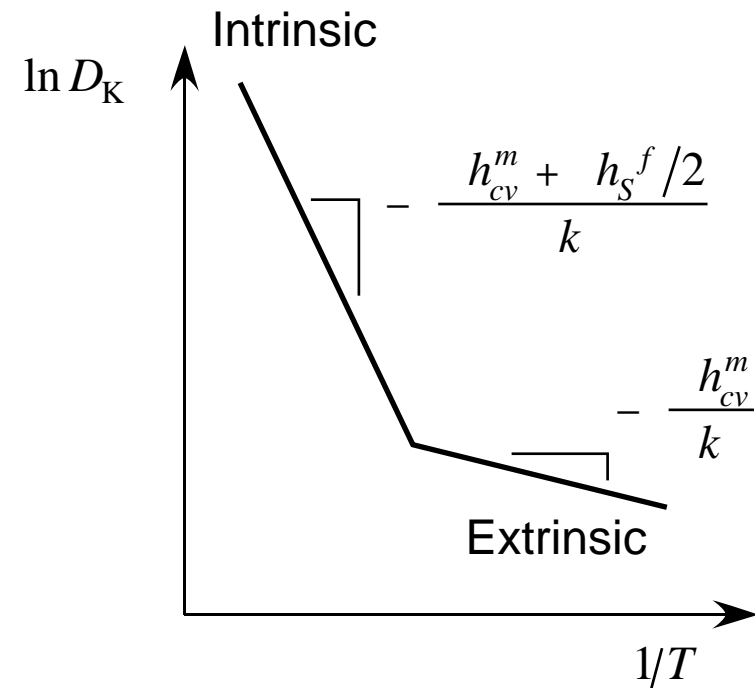**Ex***trinsic regime*: impurity concentration is high or *T* is low and thus

$$\left[V_K'\right] = \left[Ca_K^{\bullet}\right]$$

Cation diffusion in KCl with Ca impurities, cont'd:

Temperature dependencies

On the left diagram, $\ln\left[V_{\mathrm{K}}{}'\right]$ versus $1/T$, labeled "Intrinsic" with slope $-\dfrac{h_S{}^f}{2k}$, and "Extrinsic" region at $\ln\left[\mathrm{Ca_K}^{\bullet}\right]$.

On the right diagram, $\ln D_{\mathrm{K}}$ versus $1/T$, labeled "Intrinsic" with slope $-\dfrac{h_{cv}^m + h_S{}^f/2}{k}$, and "Extrinsic" with slope $-\dfrac{h_{cv}^m}{k}$.

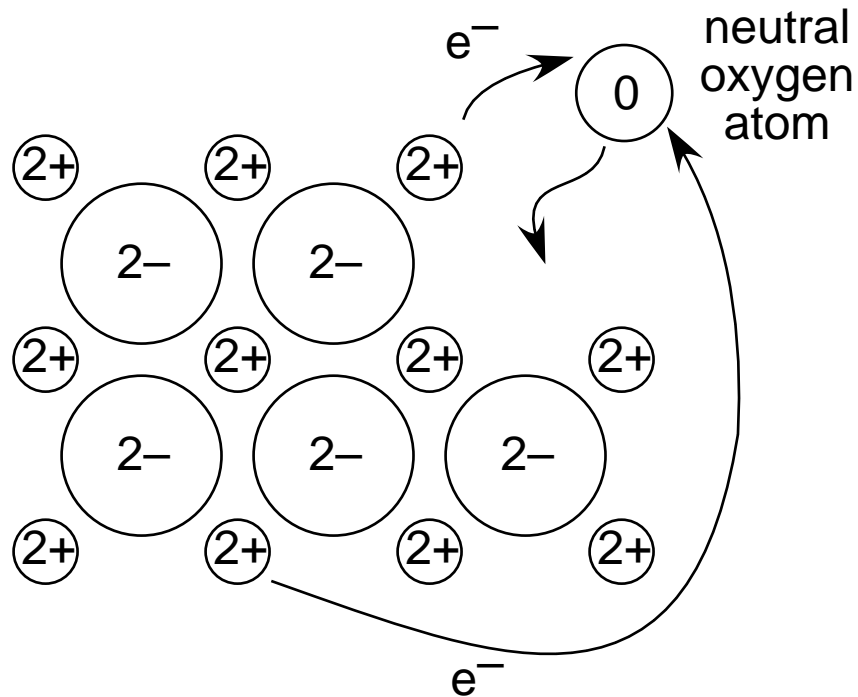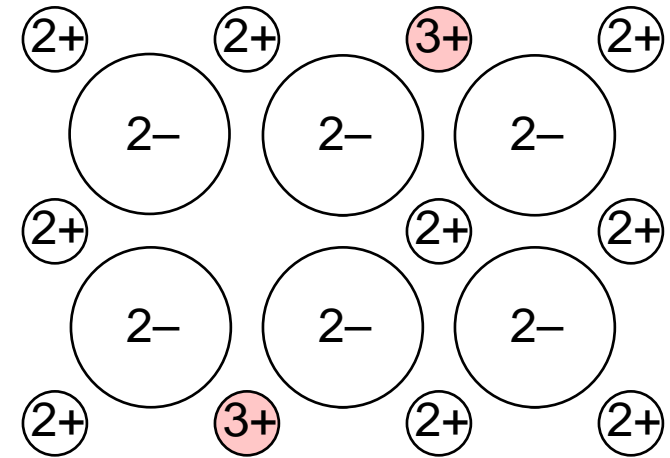**Cation vacancy concentration**   **Cation diffusivity**

• Diffusion in nonstoichiometric oxides

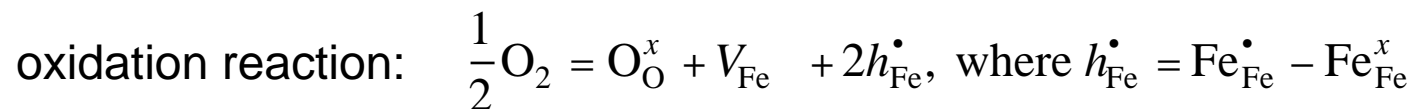— e.g., cation diffusion in FeO (note various valence states of Fe are possible)

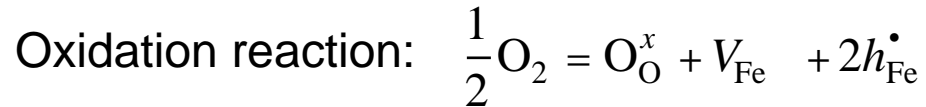FeO can be *oxidized* to make a *cation deficient* oxide $Fe_{1-x}O$

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

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

oxidation reaction: $\frac{1}{2}O_2 = O_O^x + V_{Fe} + 2h_{Fe}^{\bullet}$, where $h_{Fe}^{\bullet} = Fe_{Fe}^{\bullet} - Fe_{Fe}^x$

- **Diffusion in nonstoichiometric FeO, cont'd:**

Oxidation reaction: $\dfrac{1}{2}O_2 = O_O^x + V_{Fe} + 2h_{Fe}^{\bullet}$

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

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

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

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

$\ln D_{Fe}$

Intrinsic

$$-\frac{h_{cv}^{f}/2 + h_{cv}^{m}}{k}$$

$$-\frac{h/3 + h_{cv}^{m}}{k}$$

$$-\frac{h_{cv}^{m}}{k}$$

diffusivity varies as $(p_{O_2})^{1/6}$

Extrinsic

$1/T$
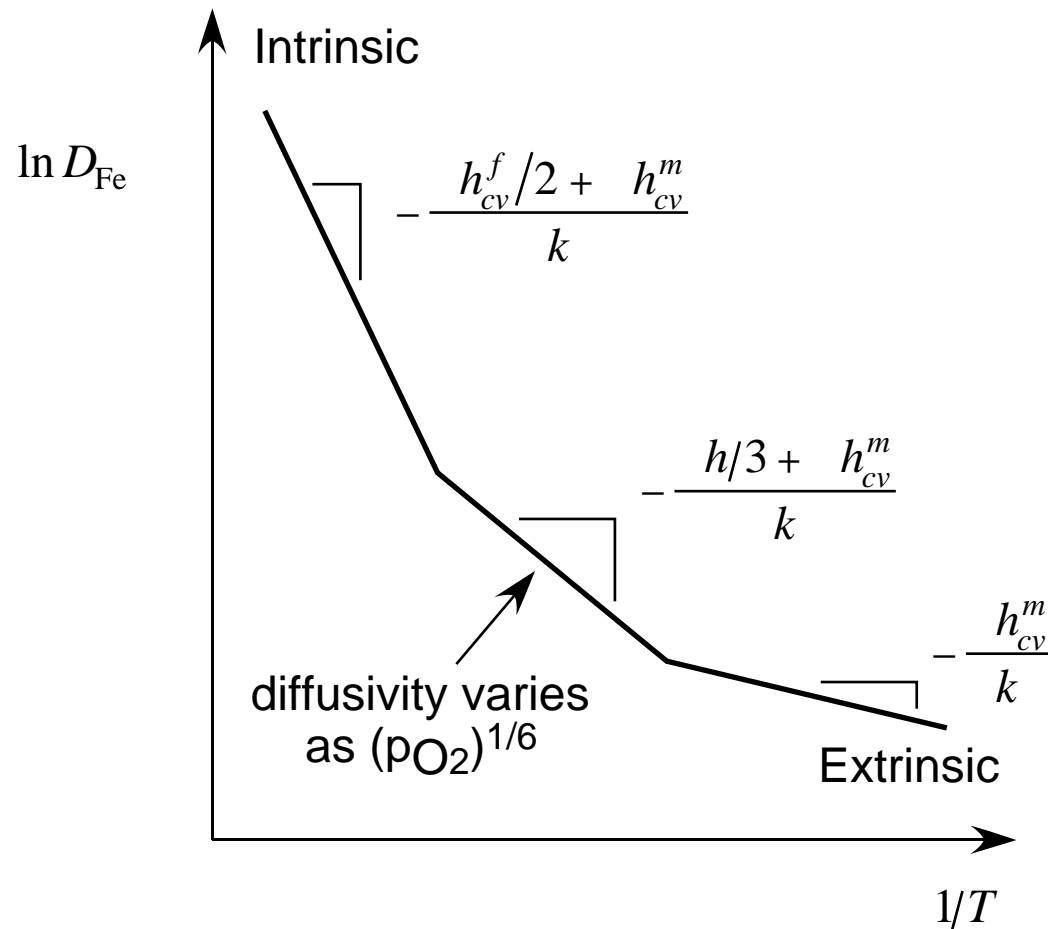
Position of middle segment will depend on oxygen pressure, hence this region will not be observable at low oxygen pressures or high impurity contents

- **Diffusion in ceramics: relevance**

  Microstructural processes

  Densification of powder compacts by sintering

  Creep deformation at high temperatures
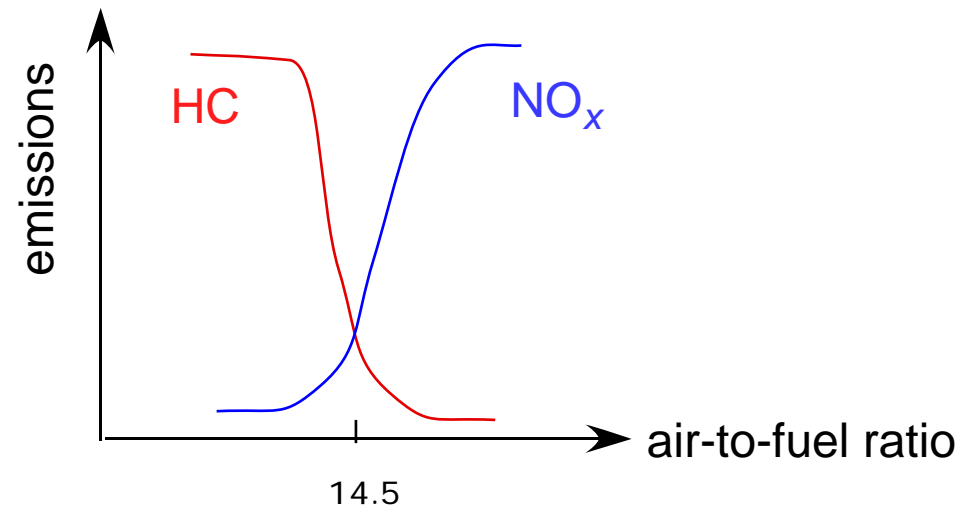
  Grain growth

  Solid–solid transformation kinetics, including oxidation of metals

  Electrical conduction

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

  The automotive oxygen sensor

sensors

The automotive oxygen sensor, cont'd:

TiO_2-based, works on *electronic* conduction that has p_{O_2} dependence

ZrO_2–Y_2O_3-based, works on electrochemical potential difference between

exhaust stream and ambient air

References for additional study:

KPIM Chapter 8

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

Allen and Thomas, *The Structure of Materials*, 1999

Section 5.1.6 on Point Imperfections in Ionic Crystals