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

\[ X^Z_Y \]

where \( X \) = what is at the site (El or V)
\( Y \) = what site is defective (El or i)
\( Z \) = effective charge at the site (\( \bullet = +; \ '-' = - \))

Examples

Intrinsic defects: Schottky and Frenkel

Defects involving impurities
Schottky disorder

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

Formation: \( \text{null} = V''_{\text{Mg}} + V^{\bullet\bullet}_{\text{O}} \)

Equilibrium: \( K_S = [V''_{\text{Mg}}] \cdot [V^{\bullet\bullet}_{\text{O}}] = \exp\left(-\frac{G^f_S}{kT}\right) \)

Charge neutrality: \([V''_{\text{Mg}}] = [V^{\bullet\bullet}_{\text{O}}]\)
Frenkel pair

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

Formation: \( \text{Li}_{\text{Li}}^x = V_{\text{Li}}' + \text{Li}_i^* \)

Equilibrium: \( K_F = [V_{\text{Li}}'] \cdot [\text{Li}_i^*] = \exp\left(-\frac{G_f^F}{kT}\right) \)

Charge neutrality: \( [V_{\text{Li}}'] = [\text{Li}_i^*] \)
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

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

- Isovalent impurities — e.g. CaO in MgO

- Incorporation: \( \text{CaO} \xrightarrow{\text{MgO}} \text{Ca}_{\text{Mg}}^\times + \text{O}_\text{O}^\times \)

- Equilibrium: \( K_S = [V''_{\text{Mg}}] \cdot [V\overset{\cdots}{\text{O}}] = \exp\left(\frac{-G^f_S}{kT}\right) \)

- Charge neutrality: \( [V''_{\text{Mg}}] = [V\overset{\cdots}{\text{O}}] \)

- Impurity does not influence point defect concentration
Extrinsic defects, cont’d

- Aliovalent impurities — e.g. CaO in ZrO₂

- Incorporation:  \[
\text{CaO} \rightarrow_{\text{ZrO}_2} \text{Ca}''_{\text{Zr}} + \text{V}^{\bullet\bullet}_\text{O} + \text{O}^\times_\text{O}
\]

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

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

- Impurities influence point defect concentration
Cation diffusion in KCl with Ca

- Impurity incorporation

\[
\text{CaCl}_2 \xrightarrow{\text{KCl}} \text{Ca}_K^+ + V'_K + 2\text{Cl}^{\text{x}}_{\text{Cl}}
\]

Schottky equilibrium

\[
K_S = [V'_K] \cdot [V^\cdot_{\text{Cl}}] = \exp\left(-\frac{G^f_S}{kT}\right)
\]

Neutrality condition

\[
[V^\cdot_{\text{Cl}}] + [\text{Ca}_K^+] = [V'_K]
\]
Diffusion in KCl with Ca, cont’d

This leads to

\[ [V_K'] = \frac{[Ca_K]}{2} \cdot \left[ 1 + \left\{ 1 + \frac{4[V_K']^2}{[Ca_K]^2} \right\}^{1/2} \right] \]

and to two regimes:

**Intrinsic:** Small impurity concentration or high T

\[ [V_K']_{\text{pure}} \gg [Ca_K], \text{ then } [V_K'] = [V_K']_{\text{pure}} \]

**Extrinsic:** High impurity concentration or low T

\[ [V_K']_{\text{pure}} \ll [Ca_K], \text{ then } [V_K'] = [Ca_K] \]
Diffusion in KCl with Ca, cont’d

- This leads to this behavior for the cation diffusivity

\[
\begin{align*}
\ln[V_K^'] & \quad \ln[D^K] \\
\ln[Ca_K^+] & \quad 1/T \\
\ln[V_K^'] & \quad \ln[D^K] \\
\ln[Ca_K^+] & \quad 1/T \\
\end{align*}
\]

Cation vacancy concentration  
Cation diffusivity

\[\begin{align*}
\ln V_K' &= -\frac{H_f^S}{2k} \\
\ln D^K &= -\left(\frac{H_{CV}^m + H_S^f/2}{k}\right) \\
\ln V_K' &= -\frac{H_f^S}{2k} \\
\ln D^K &= -\left(\frac{H_{CV}^m}{k}\right) \\
\end{align*}\]
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: $\frac{1}{2}O_2 = O_O^x + V_{Fe}^{\prime\prime} + 2h_{Fe}^{\ast}$, where $h_{Fe}^{\ast} = Fe^{\ast}_{Fe} - Fe^{x}_{Fe}$
Diffusion in nonstoichiometric FeO, cont'd:

Oxidation reaction: \[ \frac{1}{2} \text{O}_2 = \text{O}_x^O + \text{V}_{\text{Fe}}'' + 2h_{\text{Fe}}^* \]

Equilibrium constant for this reaction: \[ K_{eq} = \frac{[\text{V}_{\text{Fe}}''][h_{\text{Fe}}^*]^2}{\sqrt{p_{\text{O}_2}}} = \exp\left(-\frac{\Delta G}{kT}\right) \]

Charge neutrality: \[ 2[\text{V}_{\text{Fe}}''] = [h_{\text{Fe}}^*] \]

Cation vacancy concentration: \[ [\text{V}_{\text{Fe}}''] = (1/4)^{1/3} \exp\left(-\frac{\Delta G}{3kT}\right) \left(p_{\text{O}_2}\right)^{1/6} \]

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

\[ \ln D^\text{Fe} = \frac{H^f_{CV} / 2 + H^m_{CV}}{k} \]

\[ - \frac{H/3 + H^m_{CV}}{k} \]

- Extrinsic

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

diffusivity varies as \((P_{O2})^{1/6}\)
• 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:

\( TiO_2 \)-based, works on electronic conduction that has \( pO_2 \) dependence

\( ZrO_2-Y_2O_3 \)-based, works on electrochemical potential difference between exhaust stream and ambient air

References for additional study:


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