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DEFECTS, DISORDER AND DIFFUSION

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DEFECTS, DISORDER AND DIFFUSION

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1. Introduction

The aim of this lecture is to give an introduction to the field of 'Defects, disorder and diffusion' in crystalline solids. The microscopic defect properties of solids determine a large part of their macroscopic behavior, like mechanical properties and transport properties.

In this lecture we will focus our attention to the defect and transport properties of ceramic materials, and here mainly on oxides. To discuss the basic ideas of defect thermodynamics and transport or diffusion, simple binary or ternary oxides will be considered. Compared to these 'model systems' real ceramics are quite complicated systems with a large number of chemical components and possibly with several coexisting phases. The defect and transport properties are dicussed from a 'physico-chemical' point of view, introduced originally by Wagner and Schottky. Therefore, it is the aim of this lecture to show the importance of the chemical potentials of the components for the defect and transport properties of crystalline solids.

Only few references are given in the text of the lecture. Instead several books or reviews which were used for the preparation of this lecture are listed in the bibliography at the end. From these books or reviews detailed references can be taken.

2. Defects and Disorder

- Temperature T=0: ideal crystal with given structure

  T>0: imperfections, due to entropy

  $(G = H - T \cdot S)$

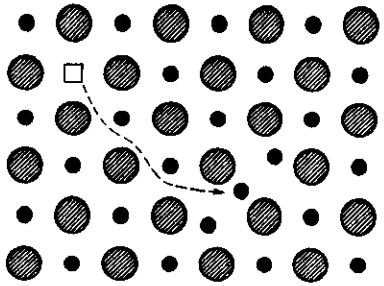
- Imperfections:

Phonons	(lattice vibrations)
Electrons, electr. holes	(electronic excitations)
Point defects	(vacancies, interstitials substitutional atoms)
1-dim. defects	(dislocations)
2-dim. defects	(grain boundaries, interfaces, surfaces)
3-dim. defects	(pores, precipitations)

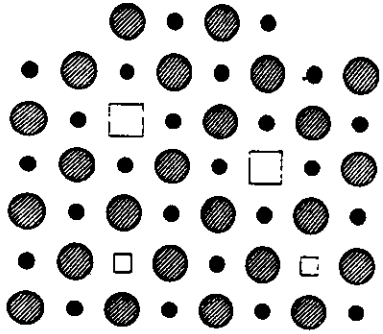
- Only electronic and point defects are in thermodynamic equilibrium (at elevated temperatures).

2.1 Types of disorder

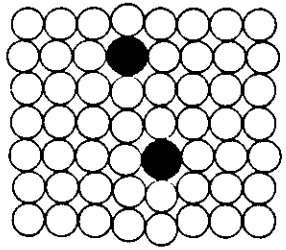
Frenkel



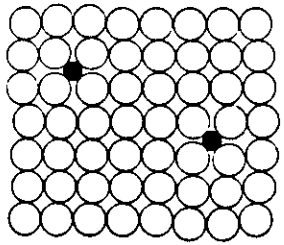
Schottky



Substitutional



Interstitial



2.2 Point defects and structure elements

Crystal with several sublattices: $\sigma = 1,.....,\Omega$

Chemical components: $k = 1,....,n$

Number of lattice points in subl. σ: Z_σ

Total number of lattice points: $Z = \Sigma Z_\sigma$

Site relation

(structure condition): $Z_\sigma : Z_\tau$ = ratio of two integers

Example: NaCl-structure $\Omega = 2$

$\sigma = 1$ anion sublattice

$\sigma = 2$ cation sublattice

$Z_1 : Z_2 = 1 : 1$

Each lattice point is occupied by a structure element:

S_σ^q

S = component k or vacancy V

σ = sublattice

q = charge

Structure elements (SE) are particles which obey the rules of statistical mechanics, i.e. it is possible to use quasichemical reactions between them.

Rules:
- Site relation
- Mass balance
- Electrical neutrality

Problem:
- Distribute the chemical components k to all sublattices σ
- Calculate the concentrations of all SE

2.3 Binary Ionic Crystals

Ions with opposite charge, no electronic defects

$n \geq 2$ $\Omega \geq 2$

Simplest case:

Binary ionic crystal AX: A = cation X = anion

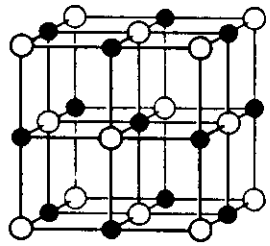
Examples are : NaCl, KCl, AgCl, NaBr, KBr, AgBr,.

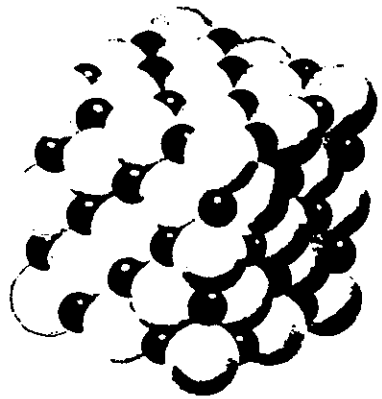
Crystal structure: NaCl (two fcc lattices)

- the cations occupy octahedral interstices (A-sites) in the fcc lattice formed by the larger anions (X-sites).

$Z_A : Z_X = 1 : 1$

- The tetrahedral interstices in the anion fcc lattice are denoted as interstitial positions I.





The charge q of the SE S_σ is taken relative to the ideal lattice (Kröger - Vink notation) and is named **effective charge:**

x = neutral
' = negative
• = positive
} relative to the ideal lattice

Structure elements in the binary ionic crystal AX:

A_A^x	$V_A^{'}$	$X_A^{''}$	Anion subl. A
X_X^x	$V_X^{\bullet}$	$A_X^{\bullet\bullet}$	Cation subl. X
V_I^x	$A_I^{\bullet}$	$X_I^{'}$	Interstitial subl. I
regular SE	irregular SE		

Point defects with small concentration:

vacancies	$V_A^{'}$, $V_X^{\bullet}$
interstitials	$A_I^{\bullet}$, $X_I^{'}$
antisite defects	$A_X^{\bullet\bullet}$, $X_A^{''}$

Cation sites are normally occupied by ions A^{1+}:

A_A^x = cation on a cation site (absolute charge: 1+ effective charge: x)

$V_A^{'}$ = vacancy on a cation site (absolute charge: 0 effective charge: ')

$X_A^{''}$ = anion on a cation site (absolute charge: 1- effective charge: '')

Anion sites are normally occupied by anions X^{1-}:

X_X^x = anion on an anion site (absolute charge: 1- effective charge: x)

$V_X^{\bullet}$ = vacancy on an anion site (absolute charge: 0 effective charge: •)

$A_X^{\bullet\bullet}$ = cation on an anion site (absolute charge: 1+ effective charge: ••)

Interstitial sites are normally empty (occupied by interstitial vacancies V_I:

V_I^x = vacancy on an interstitial pos. (absolute charge: 0 effective charge: x)

$A_I^{\bullet}$ = cation on an interstitial pos. (absolute charge: 1+ effective charge: •)

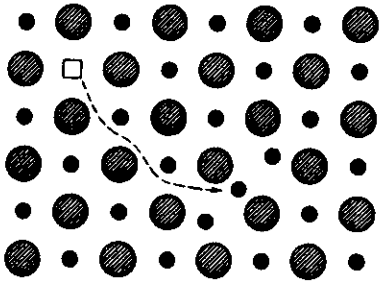
$X_I^{'}$ = anion on an interstitial pos. (absolute charge: 1- effective charge: ')

Nine SE, but only two chemical components !

Explanation:

Quasichemical reactions between the SE

Frenkel disorder



Frenkel disorder for the cations A:

$$A_A^x + V_I^x = V_A^{'} + A_I^{\cdot} \qquad (2.1)$$

Site relation: A-site + I-site = A-site + I-site

Mass balance : $M_A = M_A$

Electr. neutr: $x + x = ' + \cdot$

Chemical equilibrium:

$$\Sigma\, \tilde{\mu}(\text{reactants}) = \Sigma\, \tilde{\mu}(\text{products}) \qquad (2.2)$$

Electrochemical potential of SE S_σ^q:

$$\tilde{\mu}(S_\sigma^q) = \mu(S_\sigma^q) + q \cdot F \cdot \phi \qquad (2.3)$$

μ = chemical potential, ϕ = electrical potential

F = Faraday constant

$$\mu(S_\sigma^q) = \underbrace{\mu^{\cdot}(S_\sigma^q)}_{\text{standard potential}} + \underbrace{RT \cdot \ln(a(S_\sigma^q))}_{\text{activity}} \qquad (2.4)$$

- Ideal behavior of the structure elements: $a(S_\sigma^q) = [S_\sigma^q]$
- Number of SE S_σ^q, referred to the number of lattice points in sublattice σ: $[S_\sigma^q] = n(S_\sigma^q)/Z_\sigma$

Law of mass action for the Frenkel reaction:

$$\frac{[V_A^{'}] \cdot [A_I^{\cdot}]}{[A_A^x] \cdot [V_I^x]} = e^{-\Delta G_{FA}/RT} = K_{FA}(T) \qquad (2.5)$$

A_A^x and V_I^x are regular SE: $[A_A^x] \approx 1$ and $[V_I^x] \approx 1$

Frenkel equilibrium:

$$[V_A^{'}] \cdot [A_I^{\cdot}] = K_{FA} \qquad (2.6)$$

If cation vacancies, $V_A^{'}$, and cation interstitials, $A_I^{\cdot}$, are the only defects the electrical neutrality demands:

$$[V_A^{'}] = [A_I^{\cdot}] \qquad (2.7)$$

Thus

$$[V_A^{'}] = [A_I^{\cdot}] = (K_{FA})^{\frac{1}{2}} \qquad (2.8)$$

Frenkel disorder for the anions X:

$$X_X^X + V_I^X = V_X^\bullet + X_I^{'} \qquad (2.9)$$

Law of mass action:

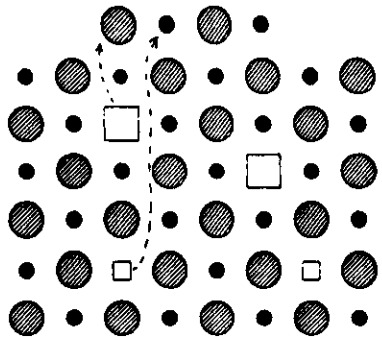
$$[V_X^\bullet] \cdot [X_I^{'}] = K_{FX} \qquad (2.10)$$

If anion vacancies, $V_X^\bullet$, and anion interstitials, $X_I^{'}$, are the only defects again the electroneutrality demands:

$$[V_X^\bullet] = [X_I^{'}] = (K_{FX})^{\frac{1}{2}} \qquad (2.11)$$

With pure Frenkel disorder the ionic crystal AX remains stoichiometric. The number of defects is only dependent on temperature T (intrinsic disorder).

Schottky disorder



$$A_A^X + X_X^X = V_A^{'} + V_X^\bullet + AX(\text{surface}) \qquad (2.12)$$

Surface: real surface or inner surface (dislocation, grain boundary).

Law of mass action for Schottky disorder:

$$[V_A^{'}] \cdot [V_X^\bullet] = K_S \qquad (2.13)$$

If Schottky disorder dominates the electrical neutrality demands:

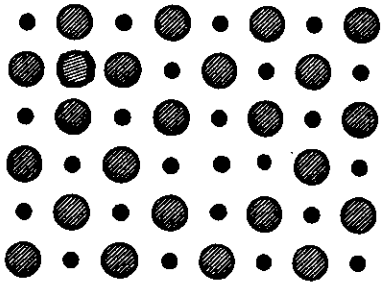
$$[V_A^{'}] = [V_X^\bullet] = (K_S)^{\frac{1}{2}} \qquad (2.14)$$

Schottky disorder involves both sublattices, the cation and the anion sublattice. The ionic crystal AX remains stoichiometric, and the number of defects is only dependent on temperature T (intrinsic disorder).

Frequently, the Schottky equilibrium (2.12) is written as:

$$0 = V_A^{'} + V_X^\bullet$$

Substitutional disorder (antisite defects)



$$A_A^X + X_X^X = A_X^{\cdot\cdot} + X_A^{''} \qquad (2.15)$$

Law of mass action

$$[A_X^{\cdot\cdot}] \cdot [X_A^{''}] = K_{sub} \qquad (2.16)$$

All these defect equilibria describe intrinsic disorder, i.e. the ionic crystal remains stoichiometric and the defect concentrations depend only on temperature (thermic disorder).

On the other hand, this means that in a really stoichiometric crystal, AX, no single chemical component, A or X, can be solved, only the 'lattice molecule' AX can be solved (Schottky equilibrium). The important consequence is that the defect properties of a really stoichiometric crystal, AX, cannot be changed by the chemical potentials of the components or the component activities a_A or a_X.

General case: All nine SE coexist.

Nine equations are needed to calculate their concentrations. Four equations are given by Eqs.(2.6), (2.10), (2.13) and (2.16):

$$[V_A^{'}] \cdot [A_I^{\cdot}] = K_{FA}$$
$$[V_X^{\cdot}] \cdot [X_I^{'}] = K_{FX}$$
$$[V_A^{'}] \cdot [V_X^{\cdot}] = K_S$$
$$[A_X^{\cdot\cdot}] \cdot [X_A^{''}] = K_{sub}$$

For small defect concentrations the concentrations of the regular structure elements, A_A^X, X_X^X and V_I^X, are (nearly) identical to one (see above):

$$[A_A^X] = 1, \quad [X_X^X] = 1, \quad [V_I^X] = 1 \qquad (2.17)$$

The 8th equation is the site relation given by the crystal structure (here NaCl) and the 9th equation is the electrical neutrality:

$$[V_A^{'}] + 2\cdot[X_A^{''}] + [X_I^{'}] = [V_X^{\cdot}] + 2\cdot[A_X^{\cdot\cdot}] + [A_I^{\cdot}] \qquad (2.18)$$

If all equilibrium constants, K, are known all defect concentrations can be calculated.

Practical point of view:

Distinguish between majority and minority point defects.

Electrical neutrality: Majority point defects consist at least of a pair of opposite charged defects

$$[V_A^{\prime}] + 2\cdot[X_A^{\prime\prime}] + [X_I^{\prime}] = [V_X^{\bullet}] + 2\cdot[A_X^{\bullet\bullet}] + [A_I^{\bullet}]$$

Example:

Majority defects: $V_A^{\prime}$ and $A_I^{\bullet}$ Frenkel disorder

$V_A^{\prime}$ and $V_X^{\bullet}$ Schottky disorder

$X_A^{\prime\prime}$ and $A_X^{\bullet\bullet}$ Antisite defects

2.4 Energy and Entropy of formation:

Equilibrium constant (law of mass action):

$$K(T) = e^{-\Delta G^{\circ}/RT} = e^{\Delta S^{\circ}/R} \cdot e^{-\Delta H^{\circ}/RT} \qquad (2.19)$$

Example: Frenkel disorder

$$[A_I^{\bullet}] = [V_A^{\prime}] = (K_F)^{\frac{1}{2}} = e^{\Delta S_F^{\circ}/2R} \cdot e^{-\Delta H_F^{\circ}/2RT}$$

$$= \text{const.} \cdot e^{-E_F/RT} \qquad (2.20)$$

$$E_F = \text{observed activation energy} \qquad (2.21)$$

$$e^{\Delta S_F^{\circ}/2R} = \text{preexponential factor} \qquad (2.22)$$

Statistical derivation

Distribute n_V vacancies to N lattice sites and n_I $(=n_V)$ interstitials to N interstitial positions.

Gibbs energy:

$$G = G_o + n_V\cdot\Delta G_V + n_I\cdot\Delta G_I - T\cdot S_c$$

$$= G_o + n\cdot(\Delta G_V + \Delta G_I) - T\cdot S_c \qquad (n = n_V = n_I)$$

$$= G_o + n\cdot\Delta G_{VI} - T\cdot S_c \qquad (2.23)$$

Configurational entropy:

$$S_c = R\cdot\ln W \qquad (2.24)$$

W = number of possible arrangements

(n=0: perfect crystal, W=1)

$$S_c = R\cdot\ln\left(\frac{N!}{(N-n_I)!\cdot n_I!}\cdot\frac{N!}{(N-n_V)!\cdot n_V!}\right) \qquad (2.25)$$

Stirling's formula: $\ln N! = n\cdot\ln N - N, \quad N \gg 1$

$$G = G_o + n\cdot\Delta G_{VI} - 2\cdot R\cdot T\cdot\left(N\cdot\ln\frac{N}{N-n} + n\cdot\ln\frac{N-n}{n}\right) \qquad (2.26)$$

Equilibrium $\left(\partial G/\partial n\right)_{p,T} = 0$ and then $N-n \approx N$

$$\Delta G_{VI} = 2 \cdot R \cdot T \cdot \ln (N/n) \qquad (2.27)$$

or

$$\frac{n}{N} = [V] = [I] = \exp\left(-\frac{\Delta G_{VI}}{2 \cdot R \cdot T}\right) \qquad (2.28)$$

Comparison with (2.20) shows that the standard Gibbs energy, ΔG_F°, for the Frenkel reaction is identical to the Gibbs energy for creating an interstitial-vacancy pair, ΔG_{VI}, as expected.

Defect Concentrations at Different Temperatures

$$\frac{n}{N} = \exp\left[-\frac{\Delta g}{2kT}\right] = \exp\left[\frac{\Delta s}{2k}\right]\exp\left[-\frac{\Delta h}{2kT}\right] \sim \exp\left(-\frac{\Delta h}{2kT}\right)$$

Defect Concentration	1 eV*	2 eV	4 eV	6 eV	8 eV
n/N at 100°C	2×10^{-7}	3×10^{-14}	1×10^{-27}	3×10^{-41}	1×10^{-54}
n/N at 500°C	6×10^{-4}	3×10^{-7}	1×10^{-13}	3×10^{-20}	8×10^{-27}
n/N at 800°C	4×10^{-3}	2×10^{-5}	4×10^{-10}	8×10^{-15}	2×10^{-19}
n/N at 1000°C	1×10^{-2}	1×10^{-4}	1×10^{-8}	1×10^{-12}	1×10^{-16}
n/N at 1200°C	2×10^{-2}	4×10^{-4}	1×10^{-7}	5×10^{-11}	2×10^{-14}
n/N at 1500°C	4×10^{-2}	1×10^{-3}	2×10^{-6}	3×10^{-9}	4×10^{-12}
n/N at 1800°C	6×10^{-2}	4×10^{-3}	1×10^{-5}	5×10^{-8}	2×10^{-10}
n/N at 2000°C	8×10^{-2}	6×10^{-3}	4×10^{-5}	2×10^{-7}	1×10^{-9}

Some Defect Energies of Formation

Compound	Reaction	Energy of Formation, Δh (eV)	Preexponential Term = $\exp(\Delta s/2k)$
AgBr	$Ag_{Ag} \rightarrow Ag_i + V_{Ag}$	1.1	30–1500
BeO	null $\rightleftarrows V_{Be}'' + V_i''$	~6	?
MgO	null $\rightleftarrows V_{Mg}'' + V_i''$	~6	?
NaCl	null $\rightleftarrows V_{Na}' + V_{Cl}^\cdot$	2.2–2.4	5–50
LiF	null $\rightleftarrows V_{Li}' + V_F^\cdot$	2.4–2.7	100–500
CaO	null $\rightleftarrows V_{Ca}'' + V_O''$	~6	?
CaF_2	$F_F \rightleftarrows V_F^\cdot + F_i'$	2.3–2.8	10^4
	$Ca_{Ca} \rightleftarrows V_{Ca}'' + Ca_i''$	~7	?
	null $\rightleftarrows V_{Ca}'' + 2V_F^\cdot$	~5.5	?
UO_2	$O_O \rightleftarrows V_O'' + O_i''$	3.0	?
	$U_U \rightleftarrows V_U'''' + U_i''''$	~9.5	?
	null $\rightleftarrows V_U'''' + 2V_O''$	~6.4	?

2.5 Binary Nonstoichiometric compounds

Nonstoichiometric compound $A_{1-\delta}X$

Nonstoichiometry $|\delta| << 1$

$\delta > 0$ cation deficit

$\delta < 0$ cation excess

Examples: CoO, NiO, MnO, FeO, ZnO,... (Mn_3O_4, Fe_3O_4, ...)

i.e. cation A^{2+} anion X^{2-} NaCl structure

Difference to pure ionic crystals:

The compound is nonstoichiometric: $n_A : n_X = 1-\delta$

However, the site relation is still: $Z_A : Z_X = 1 : 1$

This behavior cannot be explained by intrinsic disorder, like Frenkel or Schottky or substitutional disorder. There must be an extrinsic disorder.

Consider a nonstoichiometric transition metal oxide $A_{1-\delta}O$ where the metal A can exist in two valance states, A^{2+} and A^{3+}, and with NaCl-structure.

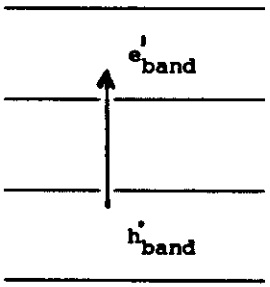
Structure elements

A_A^x	$A_A^{\bullet}$	$V_A^{''}$	cation sublattice
O_O^x		$V_O^{\bullet\bullet}$	anion sublattice
V_I^x	$A_I^{\bullet\bullet}$	$O_I^{''}$	interstitial sublattice

Substitutional disorder will be neglected because of the large size of the oxygen ions.

In addition (and in contrast to pure ionic crystals):

Electronic defects (semiconductor)



conduction band: electron e'_{band}

band gap

valence band: electron

hole $h^{\bullet}_{band}$

Total: 10 structure elements and electronic defects

Thermodynamic degrees of freedom (Gibbs phase rule):

$f = n + 2 - r$

n = number of chemical components

r = number of phases

Here: $n = 2$ and $r = 1$: $f = 3$

f = p, (total pressure)

T, (temperature)

p_{O_2} (partial pressure of oxygen)

The chemical potential of oxygen gas with partial pressure p_{O_2} is $\mu_{O_2} = \mu^{\circ}_{O_2}(T) + RT \cdot \ln(p_{O_2}/p^{\circ})$ where $\mu^{\circ}_{O_2}(T)$ is the standard chemical potential at standard pressure p°, normally p°=1 bar.

Problem: Calculate the concentrations of all defects as a function of p, T, p_{O_2}.

Normally p is fixed and only T and p_O are used as variables.

Nonstoichiometry of $A_{1-\delta}O$:

$$\delta = [V_A^{''}] - [A_I^{\bullet\bullet}] - [V_O^{\bullet\bullet}] + [O_I^{''}] \qquad (2.29)$$

2.5.1 Defect equilibria

Intrinsic disorder:

$$A_A^X + O_O^X = V_A'' + V_O^{\cdot\cdot} + AO(s) \qquad K_S = \frac{[V_A''] \cdot [V_O^{\cdot\cdot}] \cdot a_{AO}}{[A_A^X] \cdot [O_O^X]} \qquad (2.30)$$

$$A_A^X + V_I^X = V_A'' + A_I^{\cdot\cdot} \qquad K_{FA} = \frac{[V_A''] \cdot [A_I^{\cdot\cdot}]}{[A_A^X] \cdot [V_I^X]} \qquad (2.31)$$

$$O_O^X + V_I^X = V_O^{\cdot\cdot} + O_I'' \qquad K_{FO} = \frac{[V_O^{\cdot\cdot}] \cdot [O_I'']}{[O_I^X] \cdot [V_I^X]} \qquad (2.32)$$

Production of electrons and electron holes:

$$0 = e'_{band} + h^{\cdot}_{band} \qquad K_e = [e'_{band}] \cdot [h^{\cdot}_{band}] \qquad (2.33)$$

Charge transfer from A^{3+} to A^{2+}:

$$A_A^{\cdot} = A_A^X + h^{\cdot}_{band} \qquad K_2 = \frac{[A_A^X] \cdot [h^{\cdot}_{band}]}{[A_A^{\cdot}]} \qquad (2.34)$$

Extrinsic disorder:

Solve the chemical component oxygen into the crystal, and pay attention to site relation, mass balance and electrical neutrality:

$$\tfrac{1}{2} \cdot O_2(g) = O_O^X - V_O^{\cdot\cdot} + 2 \cdot (A_A^{\cdot} - A_A^X) \qquad (2.35)$$

or $\tfrac{1}{2} \cdot O_2(g) + V_O^{\cdot\cdot} + 2 \cdot A_A^X = O_O^X + 2A_A^{\cdot}, \qquad K_1 = \dfrac{[O_O^X] \cdot [A_A^{\cdot}]^2}{p_{O_2}^{\frac{1}{2}} \cdot [V_O^{\cdot\cdot}] \cdot [A_A^X]^2}$

In Eq.(2.35) the site relation is satisfied but the relation between the number of the components A and O in the crystal has changed, the crystal has become nonstoichiometric.

Electrical neutrality:

$$[A_A^{\cdot}] + 2 \cdot [A_I^{\cdot\cdot}] + 2 \cdot [V_O^{\cdot\cdot}] + [h^{\cdot}_{band}] = 2 \cdot [V_A''] + 2 \cdot [O_I''] + [e'_{band}] \qquad (2.36)$$

Eqs.(2.30)-(2.36) are seven equations for ten SE and electronic defects. The remaining three equations are the site balances in each sublattice:

$$[A_A^X] + [A_A^{\cdot}] + [V_A''] = 1 \qquad (2.37)$$

$$[O_O^X] + [V_O^{\cdot\cdot}] = 1 \qquad (2.38)$$

$$[A_I^{\cdot\cdot}] + [O_I''] + [V_I^X] = 1 \qquad (2.39)$$

Again, a general solution is possible but to complicated.

Instead:

(i) Consider only small defect concentrations, i.e. the number of the regular SE is nearly one:

$$[A_A^X] = [O_O^X] = [V_I^X] \approx 1 \qquad (2.40)$$

The activity of the pure phase $A_{1-\delta}O$ is nearly one

$$a_{AO} \approx 1 \qquad (2.41)$$

(ii) Consider only majority point defects, i.e. neglect all minority point defects in the electrical neutrality (2.36). This means that at least a pair of oppositely charged defects has to be taken.

Special case (a): Dominating Frenkel disorder of the cations

Majority point defects: $A_I^{\bullet\bullet}$ and $V_A^{''}$:

(2.36): $[A_I^{\bullet\bullet}] = [V_A^{''}]$

(2.31): $[A_I^{\bullet\bullet}] = [V_A^{''}] = (K_{FA}(T))^{\frac{1}{2}}$ (2.42)

Thus, the number of majority point defects is only dependent on temperature T and independent of the oxygen partial pressure p_{O_2}! The crystal AO is stoichiometric:

(2.29): $\delta = [V_A^{''}] - [A_I^{\bullet\bullet}] = 0$ (2.43)

Minority defects:

(2.30): $[V_O^{\bullet\bullet}] = K_S/[V_A^{''}] = K_S/(K_{FA})^{\frac{1}{2}}$ (2.44)

(2.32): $[O_I^{''}] = K_{FO}/[V_O^{\bullet\bullet}] = K_{FO}\cdot(K_{FA})^{\frac{1}{2}}/K_S$ (2.45)

(2.35): $[A_A^{\bullet}] = (K_1\cdot[V_O^{\bullet\bullet}]\cdot p_{O_2}^{\frac{1}{2}})^{\frac{1}{2}}$

$= (K_1\cdot K_S\cdot K_{FA}^{-\frac{1}{2}})^{\frac{1}{2}}\cdot p_{O_2}^{\frac{1}{4}}$ (2.46)

(2.34): $[h_{band}^{\bullet}] = K_2\cdot[A_A^{\bullet}]$

$= K_2\cdot(K_1\cdot K_S\cdot K_{FA}^{-\frac{1}{2}})^{\frac{1}{2}}\cdot p_{O_2}^{\frac{1}{4}}$ (2.47)

(2.33): $[e_{band}^{'}] = K_e/[h_{band}^{\bullet}]$

$= (K_e/K_2)\cdot(K_1\cdot K_S\cdot K_{FA}^{-\frac{1}{2}})^{-\frac{1}{2}}\cdot p_{O_2}^{-\frac{1}{4}}$ (2.48)

The number of the minority point defects, $V_O^{\bullet\bullet}$ and $O_I^{''}$, is only dependent on temperature. However, the number of the electronic defects is dependent on the oxygen partial pressure p_{O_2}. This is important for the electronic conductivity which is proportional to the number of electronic defects. The number of electrons, e', decreases with increasing oxygen partial pressure, while the number of electron holes, $h^{\bullet}$, increases with increasing p_{O_2}.

Special case (b): Cation vacancies compensated by electron holes

Majority defects: $V_A^{''}$, $A_A^{\bullet}$ and $h_{band}^{\bullet}$

(2.36): $[A_A^{\bullet}] + [h_{band}^{\bullet}] = 2\cdot[V_A^{''}]$ (2.49)

(2.34): $[h_{band}^{\bullet}] = K_2\cdot[A_A^{\bullet}]$ (2.50)

$[A_A^{\bullet}] = 2\cdot[V_A^{''}]/(1+K_2)$ (2.51)

(2.35): $[A_A^{\cdot}]^2 = K_1 \cdot [V_O^{\cdot\cdot}] \cdot p_{O_2}^{\frac{1}{2}}$

(2.30): $= K_1 \cdot K_S \cdot [V_A^{''}]^{-1} \cdot p_{O_2}^{\frac{1}{2}}$ (2.52)

(2.51), (2.52): $[V_A^{''}] = (\frac{1}{2} \cdot K_1 \cdot K_S \cdot (1+K_2)^2)^{1/3} \cdot p_{O_2}^{1/6}$ (2.53)

(2.52): $[A_A^{\cdot}] = \text{const}(T) \cdot p_{O_2}^{1/6}$ (2.54)

(2.42): $[h_{band}^{\cdot}] = \text{const}(T) \cdot p_{O_2}^{1/6}$ (2.55)

The number of majority defects is dependent on temperature, T, and increases with oxygen partial pressure, p_{O_2}, with a typical exponent 1/6. The nonstoichiometry, δ, is given by:

$$\delta = [V_A^{''}] = \text{const}(T) \cdot p_{O_2}^{1/6} \qquad (2.56)$$

Minority defects:

(2.33): $[e_{band}^{'}] = K_e/[h_{band}^{\cdot}] = \text{const}(T) \cdot p_{O_2}^{-1/6}$ (2.57)

(2.30): $[V_O^{\cdot\cdot}] = \text{const}(T) \cdot p_{O_2}^{-1/6}$ (2.58)

(2.31): $[A_I^{\cdot\cdot}] = \text{const}(T) \cdot p_{O_2}^{-1/6}$ (2.59)

(2.32): $[O_I^{''}] = \text{const}(T) \cdot p_{O_2}^{1/6}$ (2.60)

The number of all minority defects depends on temperature, T, and on oxygen partial pressure, p_{O_2}, with a typical exponent 1/6 or -1/6.

Remarks

(i) Frequently, the difference between the SE A_A (localized electron hole) and the electronic defect h_{band} (free electron hole) is dropped and both particles are denoted as 'electron hole' h . Then, the electrical neutrality takes the simple form:

$$[h^{\cdot}] = 2 \cdot [V_A^{''}] \qquad (2.61)$$

and the number of 'electron holes', $h^{\cdot}$, is given by:

$$[h^{\cdot}] = [h_{band}^{\cdot}] + [A_A^{\cdot}] = \text{const}(T) \cdot p_{O_2}^{1/6} \qquad (2.62)$$

(ii) Eqs.(2.30), (2.34) and (2.35) can be combined to an equation for the incorporation of oxygen into the crystal which contains only majority defects:

$$\frac{1}{2}O_2(g) = O_O^X + V_A^{''} + 2 \cdot h^{\cdot} \qquad \overline{K_1} = \frac{[V_A^{''}] \cdot [h^{\cdot}]^2}{p_{O_2}^{\frac{1}{2}}} \qquad (2.63)$$

The equilibrium constant $\overline{K_1}$ is a combination of the old equilibrium constants defined above: $\overline{K_1} = K_1 \cdot K_2^2 \cdot K_S$. This procedure is always possible due to the fact that any quasi-chemical reaction which satisfies the site relation, the mass balance and the electrical neutrality can be considered.

Special case (c): **Interstitial cations compensated by electrons**

Majority defects: $A_I^{\cdot\cdot}$ and e'_{band}

$$[A_I^{\cdot\cdot}] = \text{const}(T) \cdot p_{O_2}^{-1/6} \qquad (2.64)$$

$$[e'_{band}] = \text{const}(T) \cdot p_{O_2}^{-1/6} \qquad (2.65)$$

The number of majority defects depends on temperature, T, and increases with decreasing oxygen partial pressure, p_{O_2}, with a typical exponent -1/6.

Minority defects:

$[A_A^{\cdot}]$, $[h^{\cdot}_{band}]$,

$[O_I^{''}]$, $[V_A^{''}]$ $= \text{const}(T) \cdot p_{O_2}^{1/6}$ (2.66)

$$[V_O^{\cdot\cdot}] = \text{const}(T) \cdot p_{O_2}^{-1/6} \qquad (2.67)$$

The nonstoichiometry, δ, of the compound $A_{1-\delta}X$ which is here due to cation interstitials is negative, i.e. the compound exists with a cation excess:

$$\delta = -[A_I^{\cdot\cdot}]$$

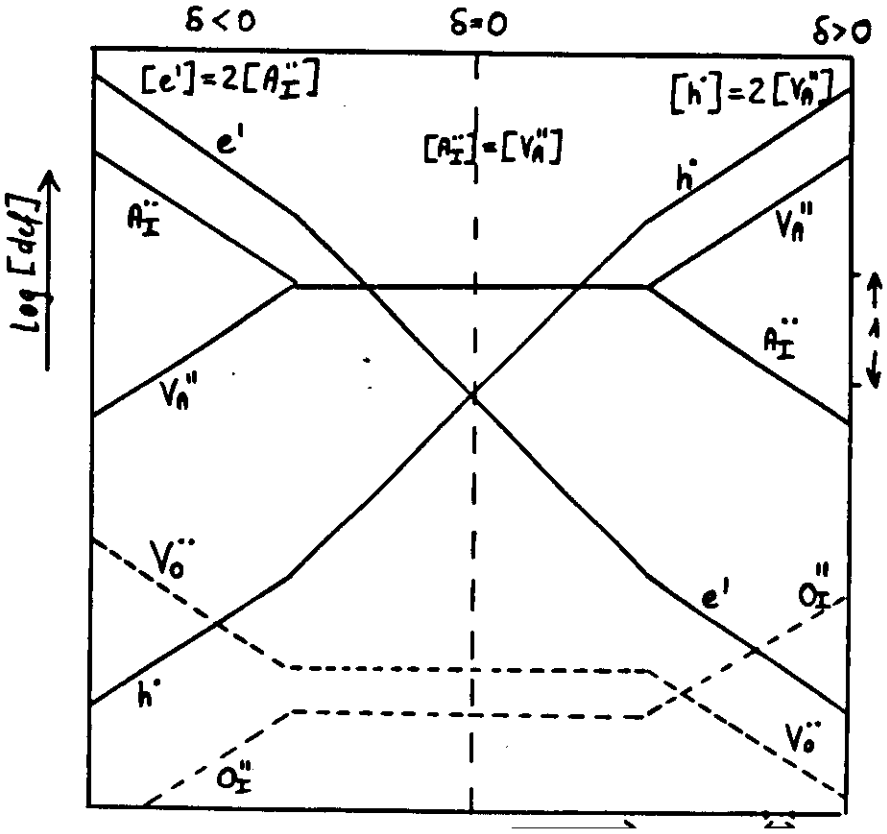
General behavior:

$$[SE] = \text{const}(T) \cdot p_{O_2}^{m} \qquad m = 0, \pm 1/4, \pm 1/6$$

$$\boxed{\log[SE] = \log(\text{const}(T)) + m \cdot \log p_{O_2}} \qquad (2.68)$$

$$\frac{d\log[SE]}{d\log p_{O_2}} = m \qquad m = 0, \pm 1/4, \pm 1/6$$

Kröger - Vink diagram $A_{1-\delta}O$



Reaktion	System	ΔH^0 (kcal/mol)	ΔS^0 (cal/K mol)
Schottkygleichgewicht	NaCl	46–49	
$A_A + X_X = V'_A + V'_X + AX$	KCl	53 (61)	
	NaBr	39	
	KBr	45,5	
	LiCl	49	
	CsCl	43	
	AgBr	109	
$(V''_{Cd} + V''_S)$	CdS	94	
$(2\,V'''_{Al} + 3\,V''_O)$	Al_2O_3	470	
$(V'_{Pb} + V'_S)$	PbS	40	
Frenkelgleichgewicht	AgCl	28 (33,8)	(20)
$A_A = V'_A + A'_i$	AgBr	24	
$(V'_F + F'_i)$	CaF_2	53–65	
$(V'_F + F'_i)$	BaF_2	43	
$(V''_O + O''_i)$	UO_2	79	
$\frac{1}{2}X_2 = X'_X + V''_{Me} + n \cdot h^{\cdot}$	AgBr	24	
$(V''_{Ni}, 2\,h^{\cdot})$	NiO	57	−8,3
$(V''_{Co}, h^{\cdot})$	CoO	13	−9
$Cd(g) = Cd_{Cd} + V''_S + 2e'$	CdS	40	
$O_O = \frac{1}{2}O_2(g) + V''_O + 2e'$	TiO_2	~110	
	Nb_2O_5	102	
	Ta_2O_5	150	
	V_2O_5	~ 30	
$UO_2 = U'_i + 2e' + O_2(g)$	UO_2	305	47,5

2.5.2 Examples CoO, ZnO and Fe_3O_4

Example (a): CoO

$Co_{1-\delta}O$ is a p-type semiconductor with a cation deficit, i.e. the nonstoichiometry, δ, is always positive. Therefore, the majority defects should be cation vacancies, V''_{Co}, compensated by electron holes, $h^{\cdot}$. If this simple model is true we would expect a variation of the nonstoichiometry, δ, with

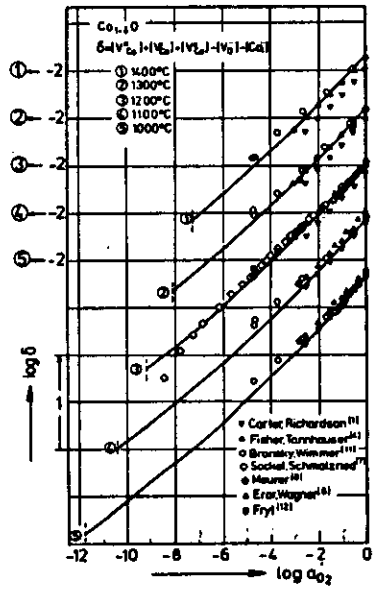
oxygen partial pressure, p_{O_2}:

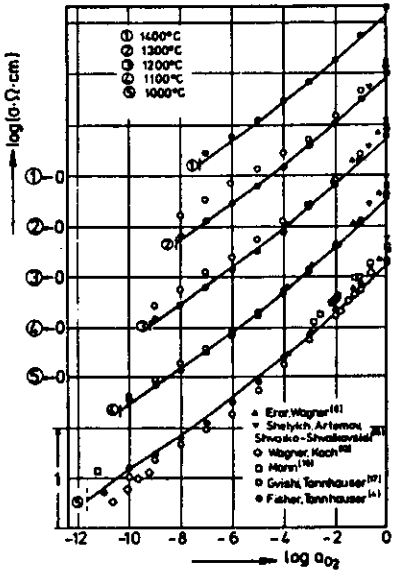
$$\frac{d\log \delta}{d\log p_{O_2}} = 1/6$$

The electronic conductivity, σ_e, is proportional to the number of electronic defects, $h^{\cdot}$, which results in an expected dependence on p_{O_2}:

$$\frac{d\log \sigma_e}{d\log p_{O_2}} = 1/6$$

However, the measured values show a dependence which is approximately given by an exponent 1/4:





Explanation: Additional quasichemical reactions between the structure elements and the electronic defects.

The observed behavior can be explained satisfactorily by the existence of three differently ionized cation vacancies compensated by electron holes.

- Incorporation of oxygen:

$$\tfrac{1}{2}O_2(g) = O_O^x + V_{Co}^{''} + 2\cdot h^{\cdot} \qquad \overline{K_1} = \frac{[V_{Co}^{''}]\cdot[h^{\cdot}]^2}{p_{O_2}^{1/2}} \tag{2.69}$$

- Formation of associates between cation vacancies, $V_A^{''}$, and electron holes, $h^{\cdot}$.

  Singly ionized cation vacancy, $V_{Co}^{'}$:

$$V_{Co}^{'} = V_{Co}^{''} + h^{\cdot} \qquad K_3 = \frac{[V_{Co}^{''}]\cdot[h^{\cdot}]}{[V_{Co}^{'}]} \tag{2.70}$$

  Neutral cation vacancy, V_{Co}^{x}:

$$V_{Co}^{x} = V_{Co}^{'} + h^{\cdot} \qquad K_4 = \frac{[V_{Co}^{'}]\cdot[h^{\cdot}]}{[V_{Co}^{x}]} \tag{2.71}$$

Together with the electrical neutrality

$$[h^{\cdot}] = [V_{Co}^{'}] + 2\cdot[V_{Co}^{''}] \tag{2.72}$$

the three equilibrium constants, $\overline{K_1}$, K_3 and K_4 can be determined by fitting the experimental data for δ and σ_e.

The results are (R.Dieckmann, Z.Phys.Chem. NF 107 (1977),189)

$$\overline{K_1} = 6.5\cdot10^{-3}\cdot\exp(-149000/RT) \tag{2.73}$$

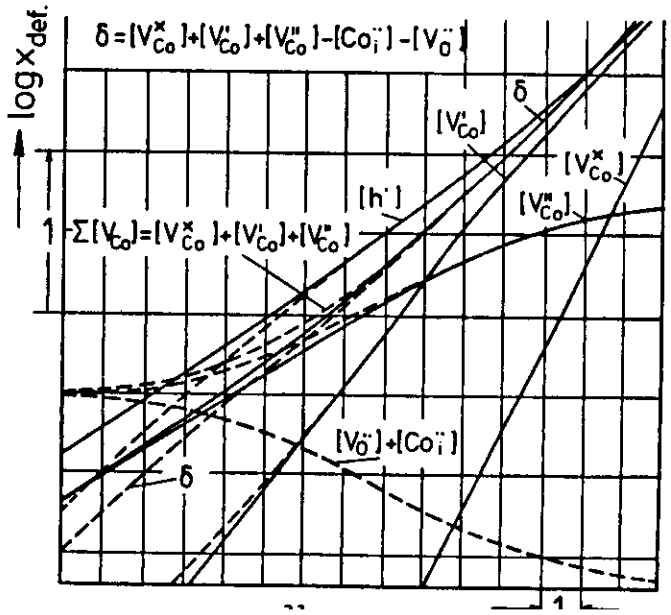
$$K_3 = 2.4\cdot\exp(-51000/RT) \tag{2.74}$$

$$K_4 = 0.17\cdot\exp(-72000/RT) \tag{2.75}$$

i.e. normally cation vacancies, $V_{Co}^{'}$, dominate with a p_{O_2}-dependence

$$[V_{Co}^{'}] = \text{const}(T)\cdot p_{O_2}^{1/4} \tag{2.76}$$

At high oxygen potential in addition neutral vacancies, V_{Co}^{x}, exist while only at low oxygen potential the 'normal' vacancies, $V_{Co}^{''}$, become important. This behavior explains the slight curvature in the log δ - log p_{O_2} and log σ_e - log p_{O_2} plots found experimentally at low oxygen potential.



Example (b): ZnO

When ZnO is heated in zinc vapor, we obtain a nonstoichiometric oxide with excess zinc, $Zn_{1+\delta}O$, which is due to Zn-interstitials:

$$Zn(g) = Zn_I^{\bullet} - V_I^{x} + e' \qquad K_I = \frac{[Zn_I^{\bullet}]\cdot[e']}{p_{Zn}} \tag{2.77}$$

With the electrical neutrality

$$[Zn_I^{\bullet}] = [e'] \tag{2.78}$$

we obtain for the nonstoichiometry, δ:

$$\delta = [Zn_I^{\bullet}] = [e'] = (K_I)^{\frac{1}{2}} \cdot p_{Zn}^{\frac{1}{2}} \tag{2.79}$$

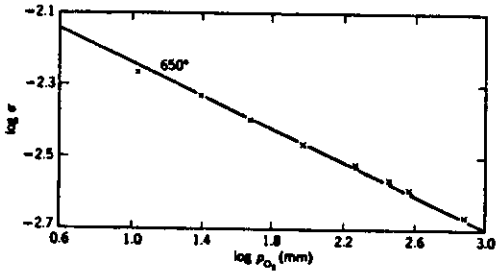
This result can be written in terms of the oxygen partial pressure, p_{O_2}, by considering the equilibrium:

$$Zn(g) + \tfrac{1}{2}\cdot O_2(g) = ZnO \qquad K_{ZnO} = p_{Zn}^{-1} \cdot p_{O_2}^{-\frac{1}{2}} \tag{2.80}$$

which yields:

$$\delta = [Zn_I^{\bullet}] = [e'] = (K_I)^{\frac{1}{2}}\cdot(K_{ZnO})^{-\frac{1}{2}} \cdot p_{O_2}^{-\frac{1}{2}} \tag{2.81}$$

This simple model is confirmed by the experimental data for the electronic conductivity, σ_e, of the n-type semiconductor ZnO.



Conductivity of ZnO as a function of oxygen pressure at 650°C. From H. H. Baumbach and C. Wagner, *Z. Phys. Chem.*, B22, 199 (1933).

Doubly ionized Zn-interstitials, Zn_I, which would result in

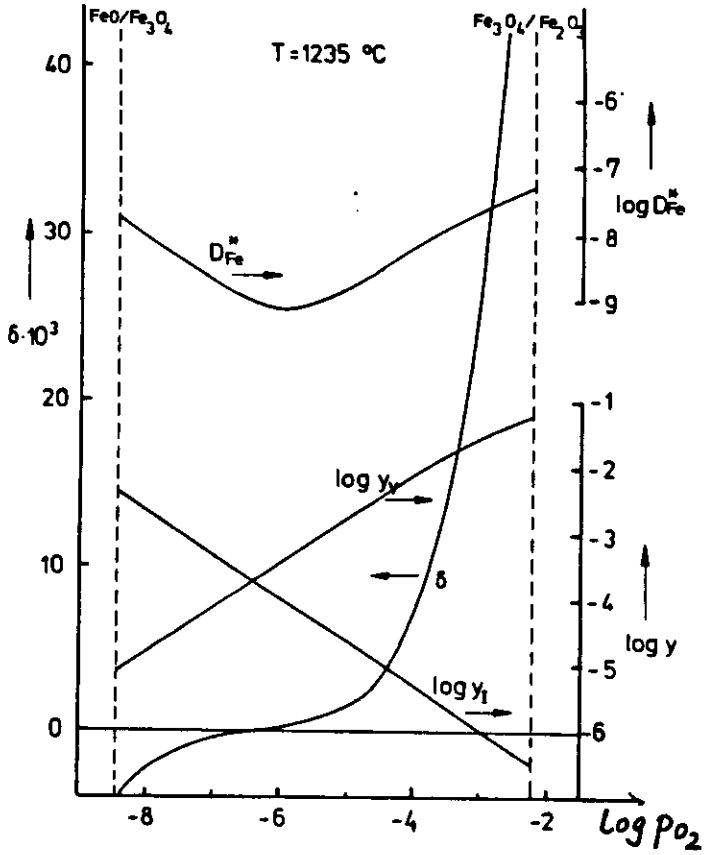
$$2\cdot[Zn_I^{\bullet\bullet}] = [e'] = \text{const}(T) \cdot p_{O_2}^{-1/6} \tag{2.82}$$

are excluded by these results.

Example (c): Fe_3O_4

Magnetite, F_3O_4, crystallizes in the spinel structure, where the cations can occupy octahedral and tetrahedral positions in the cubic closed packed lattice formed by the oxygen anions. Thermogravimetry shows that magnetite is one of the rare examples in which cation excess and cation deficit is possible, i.e. the nonstoichiometry, δ, in $Fe_{3-\delta}O_4$ can be positive and negative. This behavior can be explained satisfactorily by the existence of cation vacancies, V_{Fe}, distributed randomly over both cation sublattices, and the exist-

ence of Fe-interstitials, Fe_I. (R. Dieckmann, H. Schmalzried, Ber. Bunsenges. Phys. Chem. 81 (1977) 414)



At the stoichiometric point, δ=0, the intrinsic disorder is Frenkel disorder of the cations, while at higher oxygen potentials cation vacancies dominate and at lower oxygen poentials Fe-interstitials dominate. Fe^{2+}- and Fe^{3+}-ions are also randomly distributed over the octahedral and the tetraedral cation sublattices. Therefore, a regular SE is difficult to define so that in this case no effective charges are specified in the SE.

2.6 Impurities, Doping

As yet we have neglected the concentration of impurities compared to the concentrations of inherent defects. If small additions of foreign substances are made the equilibrium constants for the disorder types discussed above do not change. However, the site relations and the electrical neutrality change.

If for example homovalent cation impurities, B, in small concentration are present in a binary oxide AO, the corresponding SE is B_A^x and the electrical neutrality does not change. i.e. the defect properties remain unchanged.

If, however, a heterovalent impurity is present, the electrical neutrality is changed.

Example (a): If B_2O_3 is added to to an oxide AO in which cation vacancies, V_A^{II}, and electron holes, h, dominate, the electrical neutrality is as follows:

$$[h^\cdot] + [B_A^\cdot] = 2\cdot[V_A^{''}] \qquad (2.83)$$

In combination with Eq.(2.63) the number of cation vacancies, V_A, or the nonstoichiometry, δ, in the doped oxide can be calculated. If the concentration of the dopant B is large compared to the number of electron holes, $h^\cdot$, the electrical neutrality simplifies to $[B_A^\cdot] = 2\cdot[V_A^{''}]$, i.e. the nonstoichiometry, $\delta = [V_A^{''}]$, in the doped oxide is only dependent on the

dopant concentration and independent on temperature and oxygen partial pressure (region of exclusive extrinsic disorder).

Example (b): If an oxide AO_2 is doped with BO, then anion vacancies, $V_O^{\cdot\cdot}$, are produced to compensate the additional charge of the dopant, $B_A^{''}$. In this way the number of anion vacancies is totally fixed by the dopant concentration. A well known example is ZrO_2 doped with CaO which is used as a solid electrolyte with a high oxygen conductivity.

2.7 Interaction of defects, associates

When defects with opposite effective charge are present there is an attractive coulomb force between them leading to the formation of associates. In the simplest case, these associates are pairs of defects on nearest neighbor sites. For example, a vacancy pair consisting of a cation vacancy and an anion vacancy in a crystal AX containing Schottky defects is formed in the quasichemical reaction:

$$V_A' + V_X^{\cdot} = (V_A', V_X^{\cdot})^X \qquad (2.84)$$

The number of pairs is given by

$$\frac{[(V_A', V_X^{\cdot})^X]}{[V_A'] \cdot [V_X^{\cdot}]} = K_p = m \cdot e^{-\Delta G_p / RT} \qquad (2.85)$$

where m is the number of orientations of the pair (e.g. m=6

for a vacancy pair in AX with NaCl structure) and ΔG_p is the standard Gibbs energy of formation of a pair. If the vibrational entropy in ΔG_p is neglected then ΔG_p is approximately given by the coulombic energy of attraction between the oppositely charged defects. Depending on the dielectric constant, κ, and on the separation of the defects, R, this energy varies from 0.5 eV up to 2.8 eV.

By the same mechanism pairs are formed between heterovalent dopants and vacancies.

	κ	R (Å)	$-\Delta h^* \approx q_i q_j / \kappa R$ (eV)
NaCl	5.62		
$V'_{Na} - V^{\cdot}_{Cl}$		2.82	0.9
$Ca^{\cdot}_{Na} - V'_{Na}$		3.99	0.6
CaF_2	8.43		
$F'_i - V^{\cdot}_F$		2.74	0.6
$Y^{\cdot}_{Ca} - V''_{Ca}$		3.86	0.9
$Y^{\cdot}_{Ca} - V''_{Ca} - Y^{\cdot}_{Ca}$		3.86	0.4
MgO	9.8		2.8
$V''_{Mg} - V_O^{\cdot\cdot}$		2.11	2.8
$Fe^{\cdot}_{Mg} - V''_{Mg}$		2.98	1.0
$Fe^{\cdot}_{Mg} - V''_{Mg} - Fe^{\cdot}_{Mg}$		2.98	0.5
NiO	12.0		
$V''_{Ni} - V_O^{\cdot\cdot}$		2.09	2.3
$V''_{Ni} - Ni^{\cdot}_{Ni}$		2.95	0.8
$Ni^{\cdot}_{Ni} - V''_{Ni} - Ni^{\cdot}_{Ni}$		2.95	0.4
$Li'_{Ni} - Ni^{\cdot}_{Ni}$		2.95	0.4
UO_2	~15		
$O''_i - V_O^{\cdot\cdot}$		2.09	0.5

2.8 Ternary compounds

In ternary compounds an additional degree of freedom is available compared to binary compounds, i.e. apart from p and T two chemical potentials have to be fixed.

In a stoichiometric spinel, AB_2O_4, one chemical potential which is easy to control experimentally is again the oxygen partial pressure, p_{O_2}. Since the composition of the stoichiometric spinel is fixed, the other independent variable can be chosen as the activity of B_2O_3 or (AO). For simplicity, let us assume, that in the quasi-binary system AO-B_2O_3 there are no other compounds except the spinel AB_2O_4. Then the activity of B_2O_3 is equal to unity for AB_2O_4 in equilibrium with B_2O_3. For AB_2O_4 in equilibrium with AO the activity of B_2O_3 can easily be calculated from the reaction:

$$AO + B_2O_3 = AB_2O_4 \qquad K_{AB_2O_4} = (a_{AO} \cdot a_{B_2O_3})^{-1} \qquad (2.86)$$

where the equilibrium constant is given by the standard Gibbs energy of formation of spinel:

$$K_{AB_2O_4} = \exp(-G_{AB_2O_4}/RT) \qquad (2.87)$$

Taking $a_{AO} = 1$ in Eq.(2.86) yields the corresponding activity of B_2O_3:

$$a_{B_2O_3} = \exp(\Delta G_{AB_2O_4}/RT) \quad \text{when } a_{AO} = 1 \qquad (2.88)$$

Assuming the existence of interstitial cations a possible external reaction is:

$$3 \cdot AO(g) + V_I + 2 \cdot B_I^{\cdots} = B_2O_3(g) + 3 \cdot A_I^{\cdot\cdot} \qquad (2.89)$$

leading to

$$K_{ext} = a_{B_2O_3} \cdot [A_I^{\cdot\cdot}]^3 \cdot [B_I^{\cdots}]^{-2} \qquad (2.90)$$

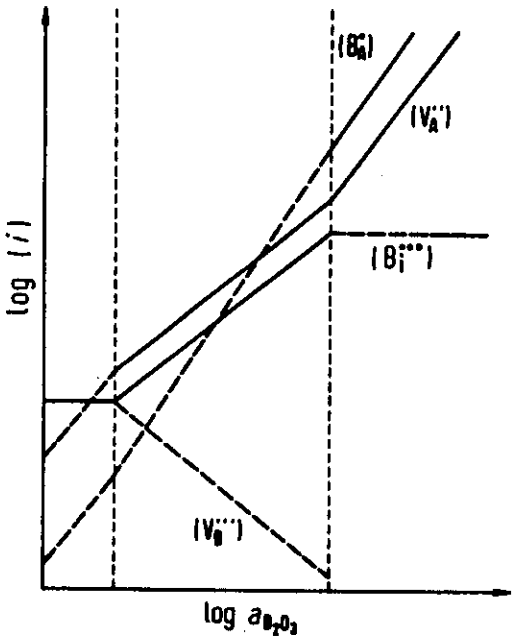
Together with Eq.(2.86) (which couples the activities of AO and B_2O_3), the site balance, the mass balance and the electrical neutrality the number of point defects can be calculated.

The result for an arbitrary type of defect i is:

$$[i] = \text{const}(T) \cdot p_{O_2}^{m} \cdot (a_{B_2O_3})^{n} \qquad (2.91)$$

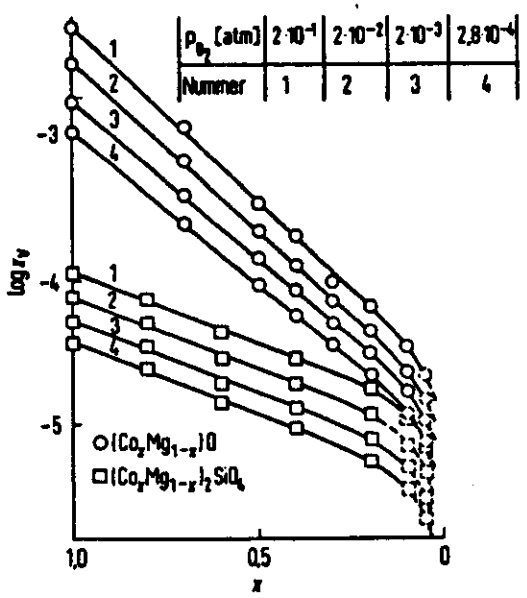
Like in binary oxides the number of defects depends on the oxygen partial pressure, p_{O_2}, with a typical exponent, m, but in addition on the B_2O_3-activity, $a_{B_2O_3}$, also with a typical exponent, n.

Concentration of point defects i in the ternary crystal AB_2O_3 at constant p_{O_2} as a function of the activity of B_2O_3. The intrinsic disorder is assumed to be Frenkel disorder in the B-sublattice: $[B_I^{\bullet\bullet\bullet}] = [V_B^{'''}]$



These considerations are valid for spinels like $MgAl_2O_4$ but they apply also to compounds with different crystal structure, such as Co_2SiO_4 with olivine structure. However the exponent n must be recalculated for each disorder type.

Finally we will discuss ternary solid solutions, $(A_xB_{1-x})O$, which exist within a large composition interval, in contrast to a spinel, AB_2O_4, discussed above. Due to this behavior, now the composition, x, can be taken as the second variable, apart from the oxygen partial pressure, p_{O_2}. Examples are the solid solutions MnO-MgO, FeO-MgO or CoO-MgO. More exactly, we should write $(A_xB_{1-x})_{1-\delta}O$, where the nonstoichiometry, δ, is now a function of p_{O_2} and of the composition, x.



These experimental data can be interpreted as follows: The standard Gibbs energy, ΔG°, for the external equilibrium (in which oxygen is solved into the crystal) is a function of the composition, x. The observed linear curves in the log δ versus x plot show that ΔG° varies linearly with composition, x.

2.9 Experiments

Possible experiments for the study of disorder in oxides $A_{1-\delta}O$ are thermogravimetry or coulometric titration. In both cases the change of the oxygen contents of the sample is measured: In the first case, via the weight change of the sample after a change of the oxygen partial pressure, and in the second case with the help of a solid state electrochemical cell by which it is possible to titrate oxygen (CaO-stabilized zirconia). However, in both cases only changes of the non-stoichiometry, δ, can be measured. Only when the compound exists really stoichiometric, i.e. when $\delta=0$ is possible, the titration curve is s-shaped and the point of inflection can serve as an absolute reference point for δ. However, even in this case the measured nonstoichiometry, δ, can be interpreted in terms of different defect models which result in the same p_{O_2}-dependence for δ.

Due to these difficulties more experimental information is needed to obtain sound defect models. One possibility was used before: the measurement of the electronic conductivity, σ_e, which is proportional to the number of electronic defects. Thus, the p_{O_2}-dependence of the electrical conductivity can help to distinguish between different defect models.

In addition, the diffusion coefficients for matter transport depend also on the oxygen partial pressure, p_{O_2}, with an exponent which is typical for the transport mechanism. How this exponent is coupled to the defect properties will be discussed in the next chapter.

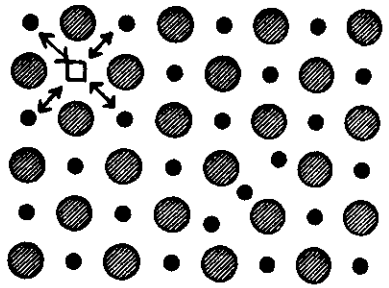
3. Diffusion

3.1 Diffusion mechanisms

Diffusion or mass transport in crystalline solids needs defects by which the ions are mobile. This concept leads to a simple distinction between two basic diffusion mechanisms.

Vacancy diffusion

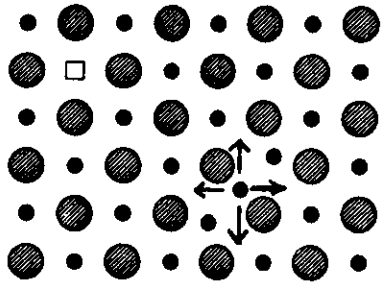
Ions which occupy regular lattice sites can jump to unoccupied lattice sites, i.e. they exchange their site with vacancies.



An equivalent point of view is to say that the vacancy has made a jump and has exchanged its site with the ion. Vacancy diffusion is the most common diffusion mechanism.

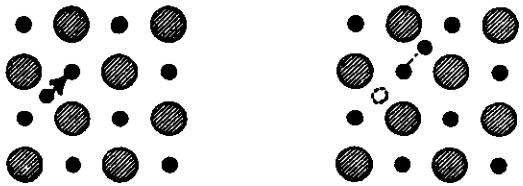
Interstitial diffusion

Interstitial ions move within the interstitial sublattice by jumping between normally unoccupied interstitial positions.



Interstitialcy diffusion

Here interstitial ions knock ions on regular lattice sites onto interstitial positions. Collinear and also non-collinear interstitialcy diffusion mechanisms are possible.

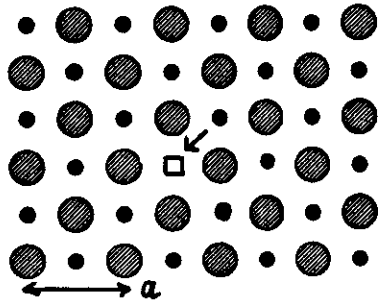


3.2 Self - diffusion

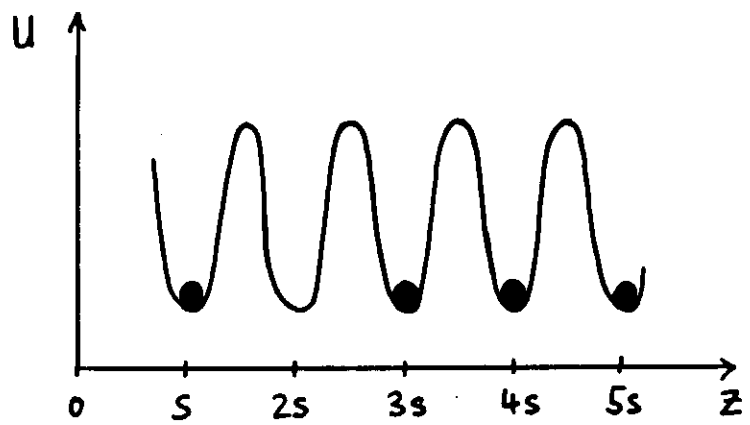
For the sake of simplicity, the following considerations will be done for a vacancy mechanism. However, the results are also valid for the other mechanisms.

Consider a binary oxide AO with cation vacancies, V_A'', as majority point defects (compensated by electron holes, $\dot{h}$). All other defects are minority defects, i.e. only the cations, A_A^x, are mobile via the vacancies. In the following discussion the site index A and the effective charge q will be dropped.

At elevated temperatures, T, and constant oxygen partial pressure, p_{O_2}, the crystal is in thermodynamic equilibrium, i.e. there are no concentration gradients for the ions A or the vacancies V. However, the ions A move randomly by exchanging with vacancies, V.



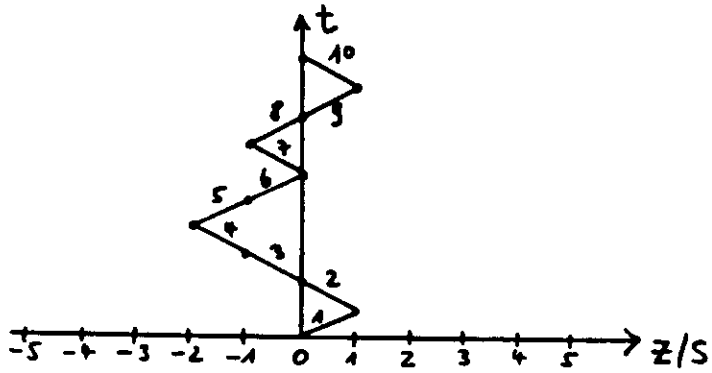
The corresponding potential for the cations looks like:



where the jump length, s, is given by: $s=a/\sqrt{2}$. Nearly all lattice sites are occupied by cations, A, and only a small amount of lattice sites, [V], is occupied by vacancies. The ions A vibrate around their equilibrium positions (Einstein- or Debey-model, phonons) with an average vibrational energy. Only if an energetic fluctuation is large enough the ion can cross the energy barrier to the next lattice site. However, a necessary condition for a jump is that this lattice site is occupied by a vacancy. Due to the fact that the ions A are not distinguishable the situation gets complicated very fast. An easier point of view is to focus on the motion of the vacancy, since these particles are strongly diluted and therefore we can follow the path of a single vacancy.

A vacancy, V, carries out a random walk, i.e. the probability of a jump in any possible direction is the same. Then, the question is: How far moves a vacancy on average in time t?

To answer this question we consider for simplicity one-dimensional diffusion of a random walker.



After time t the random walker has carried out n jumps and the corresponding total displacement, z, is:

$$\Delta z = \sum_{i=1}^{n} \Delta z_i \qquad (3.1)$$

where Δz_i is the displacement during jump i, which can only take the values $\Delta z_i = +s$ or $\Delta z_i = -s$. Because jumps to the left ($\Delta z_i=-s$) and jumps to the right ($\Delta z_i=+s$) occur with the same probability all displacements in (3.1) add up to an average total displacement, $<\Delta z>$, which is identical to zero.

$$<\Delta z> = \sum_{i=1}^{n} <\Delta z_i> = 0 \qquad (3.2)$$

However, the mean square displacement, $<(\Delta z)^2>$, is not zero:

$$<(\Delta z)^2> = <\Delta z \cdot \Delta z> = <(\sum_{i=1}^{n} \Delta z_i)\cdot(\sum_{j=1}^{n} \Delta z_j)>$$

$$= <\sum_{i=1}^{n}\sum_{j=1}^{n} \Delta z_i \cdot \Delta z_j>$$

$$< (\Delta z)^2 > = < \sum_{i=1}^{n} (\Delta z_i)^2 > + \sum_{i=1}^{n} \sum_{\substack{j=1 \\ j \neq i}}^{n} < \Delta z_i \cdot \Delta z_j > \qquad (3.3)$$

The double sum in the second term on the rhs of (3.3) adds up to zero because individual jumps i and j are uncorrelated. The first term is identical to $n \cdot s^2$, because for any jump i the quantity $(\Delta z_i)^2$ is identical to s^2. The final result is:

$$< (\Delta z)^2 > = n \cdot s^2 \qquad (3.4)$$

The mean square displacement of a random walker is proportional to the number of jumps, n, and proportional to the square of the jump distance.

Now we define a diffusion coefficient, D:

$$D = \frac{< (\Delta z)^2 >}{2 \cdot t} \qquad (3.5)$$

The jump frequency of the random walker is given by the number of jumps, n, per time,t: $\Gamma = n/t$. Thus the diffusion coefficient, D, can be written as:

$$D = \tfrac{1}{2} \cdot s^2 \cdot \Gamma \qquad (3.6)$$

In three-dimensional diffusion the factor 1/2 changes to 1/6 (six directions in space) which results in a diffusion coefficient for the vacancy:

$$D_V = (1/6) \cdot s^2 \cdot \Gamma_V \qquad (3.7)$$

Γ_V is the jump frequency of the vacancy to any of its nearest neighbor sites (=12 in the fcc structure).

The component diffusion coefficient or the self-diffusion coefficient, D_A, of the cation A can be defined in the same way:

$$D_A = (1/6) \cdot s^2 \cdot \Gamma_A \qquad (3.8)$$

where Γ_A is the jump frequency of the cation to a nearest neighbor site. However, A can jump only when the adjacent site is occupied by a vacancy. This probability is identical to the molar fraction of vacancies, $x_V = [V]$. Since a jump of an ion A corresponds to a jump of a vacancy the jump frequency Γ_A is given by the jump frequency of the vacancy, Γ_V, multiplied by the probability to find a vacancy, x_V:

$$\Gamma_A = \Gamma_V \cdot x_V \qquad (3.9)$$

Another way to obtain the relation (3.9) is the jump balance which allows also to consider the jumps of several ions via vacancies. The number of jumps of vacancies in time t must be identical to the number of jumps of ions in the same time. The number of jumps of species i is given by $n_i \cdot \Gamma_i$ where n_i is the number of species i and Γ_i the jump frequency. For our simple case of a single ion A the result is:

$$n_V \cdot \Gamma_V = n_A \cdot \Gamma_A \qquad (3.10)$$

Regarding the definition of the molar fraction of vacancies,

$$x_V = \frac{n_V}{n_A + n_V} \approx \frac{n_V}{n_A}, \qquad (n_V << n_A) \tag{3.11}$$

(3.10) is identical to (3.9). Γ_A is an effective jump frequency for all ions A. Using (3.7) the self-diffusion coefficient or component diffusion coefficient of A, D_A, can be written as:

$$D_A = D_V \cdot x_V \tag{3.12}$$

Example: $Co_{1-\delta}O$ at T = 1200°C and $p_{O_2} = 10^{-3}$ bar

$\delta = x_V \approx 10^{-3}$ and $D_V = 2 \cdot 10^{-6}\ cm^2 \cdot s^{-1}$

$a \approx 4\ \mathring{A}$

$\Gamma_V = D_V \cdot 6/a^2 = 1.5 \cdot 10^{10}\ s^{-1}$

$1/\Gamma_V = 6 \cdot 10^{-11}\ s$ time between jumps

$\Gamma_A = \Gamma_V \cdot x_V = 1.5 \cdot 10^{7}\ s^{-1}$

$< (z)^2 >^{\frac{1}{2}} = (6 \cdot D \cdot t)^{\frac{1}{2}}$ (mean square displacement)$^{\frac{1}{2}}$

after 16s: $< (z)^2 >^{\frac{1}{2}} = 140\ \mu m$ vacancy V

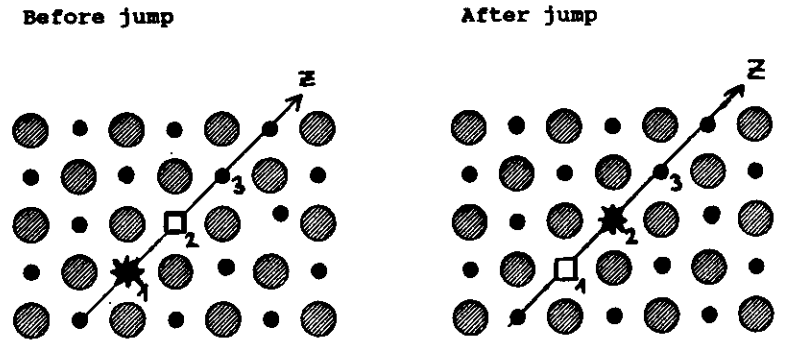
$= 4\ \mu m$ cation A

How can D_V or D_A be measured?

3.3 Tracer-diffusion

To follow the path of a single ion, A, it is necessary to mark an ion. Usually, these tracer ions are radioactive isotopes, A^*, of A which are, however, chemically identical to A. In an ideal tracer experiment, the molar fraction of the tracer ions, x_{A^*}, is negligible, even compared to the molar fraction of the (majority) defects. For this reason, the tracer ions are distinguishable and (in principle) the path of each tracer ion can be followed. Before we discuss how this is done experimentally, the microscopic diffusion step for tracer diffusion is analyzed.

Consider a situation where the tracer ion , A^*, and a vacancy, V, occupy adjacent lattice sites, 1 and 2. Now, the tracer has the possibility to jump to site 2 by exchanging sites with the vacancy.



After this jump of the tracer ion, A^*, into the positive z-direction the tracer cannot jump further into this direction because the next lattice site 3 is occupied by A. For further diffusion of the tracer into the positive z-direction the vacancy has to move to site 3 by exchanging with ions A. Therefore, the probability that the tracer jumps back to its original position 1 is larger than the probability for a jump to site 3. In other words, in contrast to the jumps of the vacancy the jumps of the tracer, A^*, are correlated, the tracer is no random walker. The jump back to the original position is not effective for diffusion which results in a mean square displacement for the tracer which is smaller than the random mean square displacement.

$$\langle(\Delta z)^2\rangle < \langle(\Delta z)^2\rangle_{random} \qquad (3.13)$$

The correlated motion of the tracer shows up in the tracer diffusion coefficient, D_A^*, in form of a geometrical correlation factor, f:

$$D_A^* = (1/6)\cdot s^2\cdot\Gamma_V\cdot x_V\cdot f \qquad (3.14)$$

With the help of (3.5) the following relation for f holds

$$f = \frac{\langle(z)^2\rangle_{correlated}}{\langle(z)^2\rangle_{random}} \qquad (3.15)$$

which can be used to calculate the correlation factor. The result is that for a given diffusion mechanism (here vacancy

mechanism) f depends only on the lattice structure in which diffusion takes place.

Lattice	Defect	f
Diamond	Vacancy	$\frac{1}{2}$
Simple cubic	Vacancy	0.6531
BCC	Vacancy	0.7272
FCC	Vacancy	0.7815
FCC	Divacancy	0.475
FCC	(100) dumb-bell interstitial	0.439
NaCl	Colinear interstitialcy	$\frac{2}{3}$
NaCl	Non-colinear interstitialcy (forward)	$\frac{11}{13}$
NaCl	Non-colinear interstitialcy (backward)	0.9643

Combining (3.14) and (3.12), allows to calculate the component diffusion coefficient of A, D_A, from the measured tracer diffusion coefficient, D_A^*, and the theoretically calculated geometrical correlation factor, f:

$$D_A^* = D_V\cdot x_V\cdot f = D_A\cdot f \qquad (3.16)$$

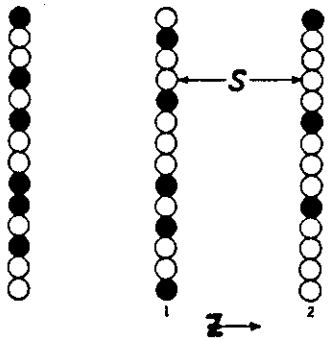
However, how can we measure the tracer diffusion coefficient in a homogeneous crystal which has been discussed up to now?

3.4 Diffusion in a concentration gradient

Diffusion in a concentration gradient is described by Fick's first law. For one-dimensional diffusion (along the z- axis) of a species with concentration, c, Fick's first law connects the flux, j, with the concentration gradient, $\partial c/\partial z$:

$$j = -D \cdot \frac{\partial c}{\partial z} \tag{3.17}$$

where D is the phenomenological diffusion coefficient. To see how this diffusion coefficient is connected to the atomistic diffusion coefficient discussed before we consider a crystal with a composition gradient along the z-axis:



The number of ions per unit area in lattice planes 1 and 2 is n_1 and n_2. We allow ions to jump left or right the jump distance s with the same probability and with the jump frequency Γ. Thus, the number of ions jumping in time dt from plane 1 into plane 2 is $\frac{1}{4} \cdot n_1 \cdot \Gamma \cdot dt$ while the number of ions jumping from plane 2 into plane 1 is $\frac{1}{4} \cdot n_2 \cdot \Gamma \cdot dt$. The number of ions which flow per time and per area through a plane between lattice planes 1 and 2 is the flux, j:

$$j = \tfrac{1}{4} \cdot (n_1 - n_2) \cdot \Gamma \tag{3.18}$$

The concentration of ions in planes 1 and 2 is given by $c_1 = n_1/s$ and $c_2 = n_2/s$ and the gradient of the concentration is $\partial c/\partial z = (c_2 - c_1)/s$, resulting in:

$$j = -\tfrac{1}{4} \cdot s^2 \cdot \Gamma \cdot \frac{\partial c}{\partial z} \tag{3.19}$$

Comparison with Fick's first law (3.17) shows that the phenomenological diffusion coefficient, D, for diffusion in a concentration gradient is identical to the microscopic diffusion coefficient of a random walker in a homogeneous crystal without concentration gradient.

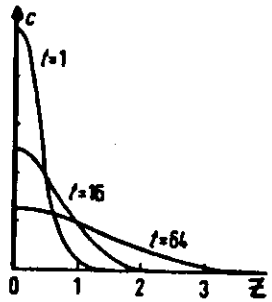
This identity allows the simple determination of (microscopic) diffusion coefficients by measuring the concentration profiles of diffusing particles. The concentration profiles, c(z,t), can be calculated by solving the continuity equation.

$$\frac{\partial c(z,t)}{\partial t} = - \frac{\partial j(z,t)}{\partial z} \tag{3.20}$$

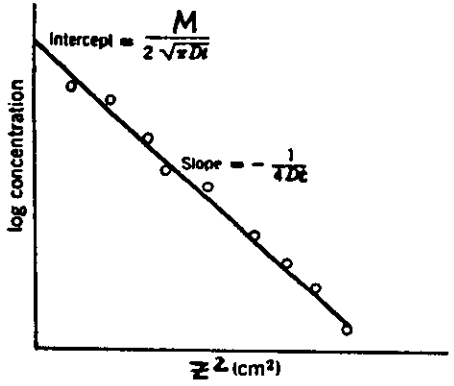
together with initial and boundary conditions.

Now, the tracer diffusion coefficient, D_A^*, can be determined easily by measuring the concentration profile, $c_A^*(z,t)$, which has developed from a thin film of tracer on the surface of the crystal under investigation. This thin film solution is a Gauss-function (M=total amount of tracer per unit area):

$$c(z,t) = \frac{M}{(\pi \cdot D_A^* \cdot t)^{\frac{1}{2}}} \cdot \exp\left(\frac{z^2}{4 \cdot D_A^* \cdot t}\right) \qquad (3.21)$$

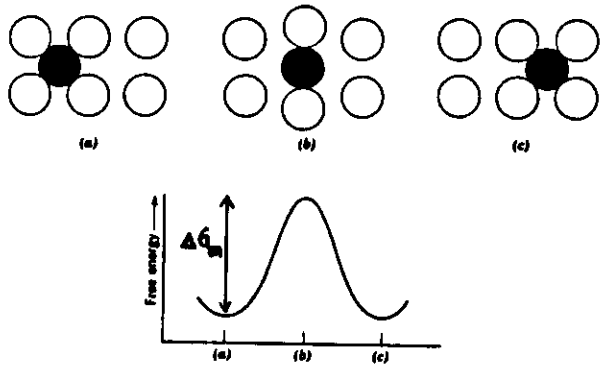


The tracer diffusion coefficient, D_A^*, is obtained from the slope of a plot log c(z,t) versus z^2.



3.5 Temperature dependence of diffusion

The jump of cations, A, from one cation site to another is a thermally activated process.



The activation Gibbs energy, ΔG_m (m=motion), to overcome the barrier between two sites, related to the thermal energy, RT, determines the fraction of ions which have sufficient energy to surmount the barrier. Thus, the diffusion coefficient is expected to have the form:

$$D_A = \text{const} \cdot \exp(-\Delta G_m / RT) \qquad (3.22)$$

From reaction rate theory one obtains the following result:

$$D_A = g \cdot \nu \cdot s^2 \cdot \exp(\Delta S_m / R) \cdot \exp(-\Delta H_m / RT) \qquad (3.23)$$

where ν is an attempt frequency to surmount the barrier which can be identified with the vibrational frequency of the atoms ($\nu \approx 10^{13}$/s). g is a geometrical factor, s is again the jump distance and ΔS_m is the entropy of motion and ΔH_m is the en-

thalpy of motion. (3.23) shows that the jump frequency, Γ, used earlier is given by:

$$\Gamma = \nu \cdot \exp(-\Delta G_m/RT) \qquad (3.24)$$

However, in this analysis it was assumed that diffusion takes place in an empty lattice. In reality, only a fraction, x_V, of the cation sites is empty, for example due to Schottky disorder. As shown in part 2.4, x_V is dependent on temperature:

$$x_V = \exp(-\Delta G_f/(2 \cdot RT))$$

where G_f is the Gibbs energy to form a cation vacancy (and an anion vacancy). The correct diffusion coefficient, D_A, for a vacancy mechanism is therefore obtained by multiplying with x_V:

$$D_A = g \cdot \nu \cdot s^2 \cdot \exp\left(-\frac{\Delta G_m + \frac{1}{2} \cdot \Delta G_f}{RT}\right)$$

$$= g \cdot \nu \cdot s^2 \cdot \exp\left(\frac{\Delta S_m + \frac{1}{2} \cdot \Delta S_f}{R}\right) \cdot \exp\left(-\frac{\Delta G_m + \frac{1}{2} \cdot \Delta G_f}{RT}\right) \qquad (3.25)$$

Thus, the diffusion coefficient can be expressed as:

$$D_A = D_A^* \cdot \exp(-Q/RT) \qquad (3.26)$$

where Q is the activation energy which can be determined experimentally from the slope of a ln D_A versus 1/T plot (Arrhenius plot).

Values of the Schottky Formation Enthalpy ΔH_s and the Cation Jump Enthalpy ΔH^* of Several Halides

Substance	ΔH_s (eV)	ΔH^* (eV)
LiF	2.34	0.70
LiCl	2.12	0.40
LiBr	1.8	0.39
LiI	1.34, 1.06	0.38, 0.43
NaCl	2.30	0.68
NaBr	1.68	0.80
KCl	2.6	0.71
KBr	2.37	0.67
KI	1.60	0.72
CsCl	1.86	0.60
CsBr	2.0	0.58
CsI	1.9	0.58
TlCl	1.3	0.5
$PbCl_2$	1.56	
$PbBr_2$	1.4	

Enthalpy and Entropy Values for Diffusion in KCl

Schottky defect formation:	
Enthalpy ΔH_s (eV)	2.6
Entropy $\Delta S_s/k$	9.6
Potassium ion migration:	
Enthalpy ΔH_+^* (eV)	0.7
Entropy $\Delta S_+^*/k$	2.7
Chlorine ion migration:	
Enthalpy ΔH_-^* (eV)	1.0
Entropy $\Delta S_-^*/k$	4.1

Source. S. Chandra and J. Rolfe, *Can. J. Phys.*, 48, 412 (1970).

3.6 Irreversible thermodynamics

Fick's first law (3.17) is a special case of more general transport equations which can be derived within the framework of linear irreversible thermodynamics.

The starting point is to calculate the rate by which entropy is produced during an irreversible process. As a result, the entropy production, σ, can be written as:

$$\sigma \cdot T = \Sigma_i \, j_i \cdot X_i \qquad (3.27)$$

where the sum extends over all irreversible processes. j_i is

a generalized flux (mass transport, energy transport, chemical reaction rate,...) and X_i is the conjugated generalized thermodynamic 'force'. To every irreversible process corresponds a special 'force':

Irreversible process	Flux	Force
Heat transport	j_q	$X_q = -\nabla T/T$
Mass transport of species i	j_i	$X_i = F_i - T\cdot\nabla(\mu_i/T)$
Chemical reaction	$(dc/dt)_{react}$	$X_{react} = \Sigma_k \nu_k\cdot\mu_k$

Here F_i is a 'true' force acting on species i, like an electrical force. For constant temperature, T, the thermodynamic force for mass transport simplifies to:

$$X_i = F_i - \nabla\mu_i \qquad (3.28)$$

and if only electrical forces, $F_i = -q_i\cdot F\cdot\nabla\phi$, where ϕ is the electric potential and F the Faraday constant, are considered then the thermodynamic force, X_i, for mass transport is given by the negative gradient of the electrochemical potential of species i.

$$X_i = -\nabla(\mu_i + q_i\cdot F\cdot\phi) = -\nabla\tilde{\mu}_i \qquad (3.29)$$

In the linear regime, i.e. for 'small' forces, the flux, j_i, of species i (i=1,...,n) is proportional to the thermodynamic forces, X_i, with a transport coefficients, L_{ij}:

$$j_i = \Sigma_j L_{ij}\cdot X_j \qquad i=1,....,n \qquad (3.30)$$

By definition, the transport coefficients are independent of the forces. Therefore, the gradients in the chemical potentials of the diffusing species are the true forces and not the concentration gradients like in Fick's first law. In addition, (3.30) states that the flux of species i is not only due to the force X_i but also due to all other forces. These 'cross-effects' are described by the cross coefficients, L_{ij}, for which Onsager's reciprocal relations hold:

$$L_{ij} = L_{ji} \qquad i,j=1,....,n \qquad (3.31)$$

A rough estimate of the transport coefficients is possible by neglecting the cross-coefficients, $L_{ij}=0$ (i=j), resulting in:

$$j_i = L_{ii}\cdot X_i \qquad (3.32)$$

On the other hand, the mobility, b_i, of species i is defined as its velocity, v_i, per unit force, resulting in a flux

$$j_i = c_i\cdot v_i = c_i\cdot b_i\cdot X_i \qquad (3.33)$$

Using the Nernst-Einstein relation

$$D_i = b_i \cdot R \cdot T \tag{3.34}$$

the transport coefficient L_{ii} can be written as:

$$L_{ii} = \frac{D_i \cdot c_i}{R \cdot T} \tag{3.35}$$

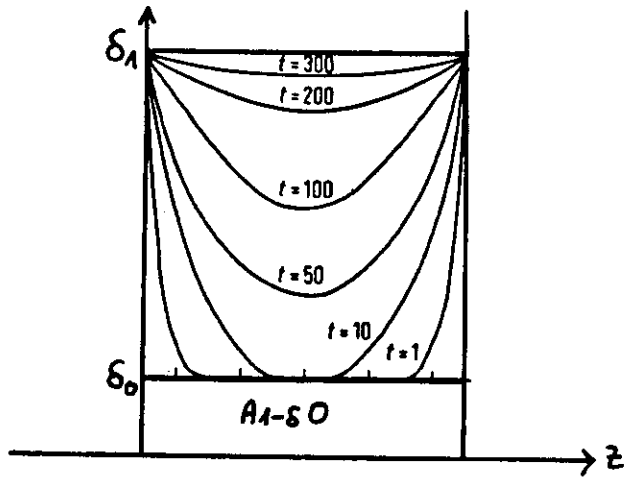
The transport coefficient of species i, L_{ii}, is given by the product of its diffusion coefficient, D_i, and its concentration, c_i, referred to the thermal energy, RT. Apart from correlation effects this result remains true if the off-diagonal elements in the transport matrix L are not neglected.

3.7 Chemical diffusion in a binary oxide AO

Consider a binary metal deficient oxide, $A_{1-\delta}O$, with cation vacancies, V_A'', as majority point defects compensated by electron holes, $h^{\cdot}$ (CoO, NiO, MnO), which is equilibrated at elevated temperatures and at a certain p_{O_2}. If the oxygen partial pressure of the surrounding atmosphere is increased an oxidation process carries on in which cations, $A_A^{\times}$, flow to the surface and cation vacancies flow to the interior of the crystal. As a result the nonstoichiometry, δ, increases from its original value, δ_o, to a final value, δ_1, corresponding to the new oxygen partial pressure p_{O_2}. This process is called chemical diffusion and the flux of cations A is given by

$$j_A = -\tilde{D} \cdot \nabla c_A \tag{3.36}$$

where $\tilde{D}$ is the chemical diffusion coefficient.



How is the chemical diffusion coefficient, $\tilde{D}$ connected to the other diffusion coefficients?

The thermodynamic force exerted in this experiment is a gradient in the chemical potential of oxygen, $\nabla \mu_{O_2}$. However, due to the equilibrium

$$A + \tfrac{1}{2} \cdot O_2(g) = AO, \qquad \mu_A + \tfrac{1}{2} \cdot \mu_O = \mu_{AO}^{\cdot} \tag{3.37}$$

where $\mu_{AO}^{\cdot}$ is the constant standard potential of the pure phase AO, the gradients of the chemical potentials of oxygen and A are not independent:

$$\nabla \mu_A = -\tfrac{1}{2} \cdot \nabla \mu_{O_2} \tag{3.38}$$

There is only a single thermodynamic force in this experiment given by (3.38) and therefore the flux of the mobile cation can be written as:

$$j_A = -L_{AA} \cdot \nabla \mu_A \qquad (3.39)$$

where the transport coefficient is given by (see (3.35)):

$$L_{AA} = D_A \cdot c_A / RT \qquad (3.40)$$

The force, $\nabla \mu_A$, exerted on the chemical component, A, needs more attention, because the component A does not exist within the crystal. As discussed earlier, within the crystal only structure elements exist. This problem can be solved, by regarding the solution of component A into the crystal:

$$A = A_A^X - V_A^{''} - 2 \cdot h^{\cdot} \qquad (3.41)$$

Eq.(3.41) satisfies the site relation, the mass balance and the electrical neutrality. If equilibrium is established for (3.41) we can write for the chemical potential of component A:

$$\mu_A = \mu(A_A^X) - \mu(V_A^{''}) - 2 \cdot \mu(h^{\cdot}) \qquad (3.42)$$

where the chemical potentials on the rhs are the chemical potentials of SE and electronic defects. Each of them can be written as the sum of a standard potential and an activity term:

$$\mu(i) = \mu^{\cdot}(i) + RT \cdot \ln a(i) \qquad (3.43)$$

Since the molar fraction of vacancies, $x(V_A^{''})$, is very small compared to the molar fraction of cations, $x(A_A^X)$, both particles can be regarded as an ideal solution within the cation sublattice, i.e. their activities are given by their molar fractions. The activity of the electron holes, $a(h^{\cdot})$, is also given by their molar fraction, $x(h^{\cdot})$, provided the number of holes is not too large. Now the chemical potential of the component A can be written as:

$$\mu_A = \mu^{\cdot}(A_A^X) - \mu^{\cdot}(V_A^{''}) - 2 \cdot \mu^{\cdot}(h^{\cdot}) + RT \cdot \left(\ln x(A_A^X) - \ln x(V_A^{''}) - 2 \cdot \ln x(h^{\cdot}) \right) \qquad (3.44)$$

Regarding that $x(A_A^X) \approx 1$ and $x(h^{\cdot}) = 2 \cdot x(V_A^{''}) \ll 1$, the gradient of μ_A can be written as:

$$\nabla \mu_A = - RT \cdot \left(\nabla \ln x(V_A^{''}) + 2 \cdot \nabla \ln(2 \cdot x(V_A^{''})) \right) \approx - RT \cdot 3 \cdot \nabla \ln x(V_A^{''}) \qquad (3.45)$$

Using $L_{AA} = D_A \cdot c_A / RT$ and $D_A = D_V \cdot x_V$ the final result for the flux of A is ($c_A = x(A_A)/V_m$, V_m = molar volume):

$$j_A = - L_{AA} \cdot \nabla \mu_A = - 3 \cdot D_V \cdot \nabla c_A \qquad (3.46)$$

Comparison with (3.36) shows that the chemical diffusion

coefficient, $\tilde{D}$, which describes diffusion of the cations, A, under the influence of a thermodynamic force is given by:

$$\tilde{D} = 3 \cdot D_V \qquad (3.47)$$

Due to the conservation of lattice sites in the cation sublattice the flux of cations, j_A, and the flux of vacancies, j_V, are not independent:

$$j_A + j_V = 0 \qquad (3.48)$$

resulting in:

$$j_V = - \tilde{D} \cdot \nabla c_V \qquad (3.49)$$

In a binary oxide, $A_{1-\delta}O$, chemical diffusion of cations and of vacancies is described by a single chemical diffusion coefficient, $\tilde{D}$.

The chemical diffusion coefficient, $\tilde{D}$, is larger than the self-diffusion coefficient of the vacancies, D_V, by a factor of 3. This enhancement factor is due to the fact that the oxide AO is a semiconductor with mobile electronic defects, $h^{\cdot}$. During a chemical diffusion experiment electrical neutrality prevails, i.e. there is no electric flux through the sample. Thus the electronic defects have to move with the charged vacancies:

$$j_{h^{\cdot}} - 2 \cdot j_{V_A^{''}} = 0 \qquad (3.50)$$

Because the electron holes, $h^{\cdot}$, have a higher mobility than the vacancies, $V_A^{''}$, they 'try to move faster' which results in an inner electrical field, called **Nernst field**. The corresponding electrical potential is called **diffusion potential**. This diffusion potential slows down the motion of the faster electron holes and enhances the motion of the slower cation vacancies. The exact calculation of the enhancement factor shows that it is identical to $1 + \alpha$, where α is the effective charge of the dominating cation vacancy. Thus,

$$D = D_V \cdot (1+\alpha), \qquad V_A^{\alpha\prime} \text{ dominates} \qquad (3.51)$$

If cation vacancies, $V_A^{'}$, dominate, as this was shown for the case of CoO, then $\alpha = 1$ and the enhancement factor for chemical diffusion is 2.

Remark:

During tracer diffusion there are no external forces, and the crystal is chemically homogeneous, particularly, $\nabla x(V_A) = 0$. However, the same formalism as above can be used:

$$j_{A^*} = - L_{A^*A^*} \cdot \nabla \mu_{A^*} = - (D_A^* \cdot c_{A^*}/RT) \cdot \nabla \mu_{A^*} \qquad (3.52)$$

$$A^* = (A^*)_A^X - V_A^{''} - 2 \cdot h^{\cdot} \qquad (3.53)$$

$$\nabla \mu_{A^*} = RT \cdot \nabla \ln x_{A^*} \qquad (3.54)$$

$$j_{A^*} = - D_A^* \cdot \nabla c_{A^*} \qquad (3.55)$$

3.8 Interdiffusion

Consider a diffusion couple of AO and BO where the binary 'components', AO and BO, form a complete solid solution, $(A_{1-x}B_x)O$. The experiment is carried out at constant temperature, T, and in an atmosphere with constant oxygen partial pressure p_O . The cations, A and B, are mobile via cation vacancies while oxygen is immobile. At time, t=0, we have the following situation:

What are the interdiffusion profiles of AO and BO ?

From linear irreversible thermodynamics we know:

$$\sigma \cdot T = \Sigma\, j_k \cdot X_k = j_A \cdot X_A + j_B \cdot X_B \qquad (3.56)$$

with $X_A = -\nabla \mu_A$ and $X_B = -\nabla \mu_B$. The fluxes can be written as:

$$j_A = -L_{AA} \cdot \nabla \mu_A - L_{AB} \cdot \nabla \mu_B \qquad (3.57)$$

$$j_B = -L_{BA} \cdot \nabla \mu_A - L_{BB} \cdot \nabla \mu_B \qquad (3.58)$$

The flux of the cations, $j_A + j_B$, is compensated by a flux of vacancies, j_V (conservation of lattice sites):

$$j_A + j_B + j_V = 0 \qquad (3.59)$$

To proceed two assumptions are necessary:

(i) Equilibrium for the oxidation of A to AO and B to BO:

$$A = AO - \tfrac{1}{2} \cdot O_2 \qquad \nabla \mu_A = \nabla \mu_{AO} - \tfrac{1}{2} \cdot \nabla \mu_O$$

$$= \nabla \mu_{AO} \qquad (3.60)$$

$$B = BO - \tfrac{1}{2} \cdot O_2 \qquad \nabla \mu_B = \nabla \mu_{BO} - \tfrac{1}{2} \cdot \nabla \mu_O$$

$$= \nabla \mu_{BO} \qquad (3.61)$$

(ii) The mixed oxide, $(A_{1-x}B_x)O$, which forms during interdiffusion is an ideal mixture of the binary 'components' AO and BO, with $x_{AO} = x_A$ and $x_{BO} = x_B = 1-x_A$, i.e.

$$\mu_{AO} = \mu_{AO}^{\cdot} + RT \cdot \ln x_A \quad \text{and} \quad \mu_{BO} = \mu_{BO}^{\cdot} + RT \cdot \ln x_B \qquad (3.62)$$

Now the flux j_A in (3.57) can be written as:

$$j_A = -L_{AA} \cdot RT \cdot \frac{\nabla x_A}{x_A} - L_{AB} \cdot RT \cdot \frac{\nabla x_B}{x_B}$$

$$= -RT \cdot \left(\frac{L_{AA}}{x_A} - \frac{L_{AB}}{x_B} \right) \cdot \nabla x_A, \qquad (x_A + x_B = 1)$$

$$= -RT \cdot \left(\frac{L_{AA}}{c_A} - \frac{L_{AB}}{c_B} \right) \cdot \nabla c_A \qquad (3.63)$$

where $c_A = x_A/V_m$ and $c_B = x_B/V_m$ are the concentrations of A and B (V_m = molar volume). Comparing (3.63) with Fick's first

law we can define a component diffusion coefficient, D_A:

$$D_A = RT\cdot\left(\frac{L_{AA}}{c_A} - \frac{L_{AB}}{c_B}\right) \qquad (3.64)$$

If the cross coefficient, L_{AB}, is neglected we obtain again the relation between D_A and L_{AA} found in (3.35).

In the same way the flux j_B is given by:

$$j_B = -D_B\cdot\nabla c_B \qquad (3.65)$$

where the component diffusion coefficient of B, D_B, is defined as:

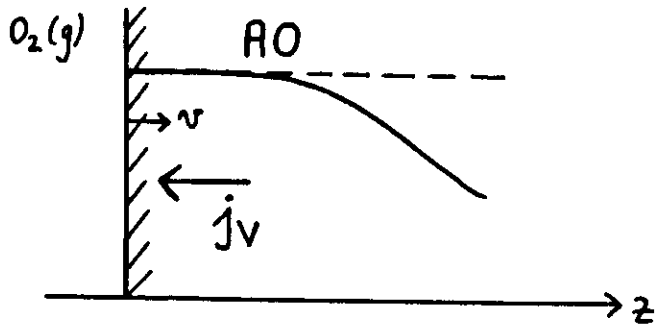
$$D_B = RT\cdot\left(\frac{L_{BB}}{c_B} - \frac{L_{BA}}{c_A}\right) \qquad (3.66)$$

Generally, the diffusion coefficients, D_A and D_B, are not identical resulting in a non-vanishing flux of vacancies through the crystal:

$$j_V = -j_A - j_B = (D_A - D_B)\cdot\nabla c_A \qquad (3.67)$$

This induced vacancy flux can 'relax' at the surfaces of the crystal provided that the number of inner surfaces is negligible. At the surface where vacancies arrive the following reaction carries on:

$$AO + V_A^{''} + 2\cdot h^{\cdot} = A_A^{x} + \tfrac{1}{2}\cdot O_2(g) \qquad (3.68)$$



Lattice planes disappear and the surface of the crystal moves relative to the lattice frame with a velocity:

$$v = -V_m\cdot j_V \qquad (3.69)$$

Experimentally, the concentration profiles of A or B are measured relative to the surfaces which have shifted during the experiment. Therefore, we transform to a new reference frame which moves with velocity v relative to the lattice frame. In this reference frame the flux of A is:

$$\begin{aligned} {}_vj_A &= j_A - c_A\cdot v = j_A + c_A\cdot V_m\cdot j_V \\ &= j_A + x_A\cdot(-j_A - j_B) \\ &= (1 - x_A)\cdot j_A - x_A\cdot j_B \\ &= -x_B\cdot D_A\cdot\nabla c_A + x_A\cdot D_B\cdot\nabla c_B \\ &= -(x_B\cdot D_A + x_A\cdot D_B)\cdot\nabla c_A \end{aligned} \qquad (3.70)$$

In the same way, the flux of B can be calculated as:

$$ {}_{v}j_B = -(x_A \cdot D_B + x_B \cdot D_A) \cdot \nabla c_B \qquad (3.71) $$

Both fluxes, j_A as well as j_B, are characterized by the same interdiffusion coefficient, $\tilde{D}$:

$$ \tilde{D} = x_A \cdot D_B + x_B \cdot D_A \qquad (3.72) $$

This relation for the interdiffusion coefficient is called Darken relation.

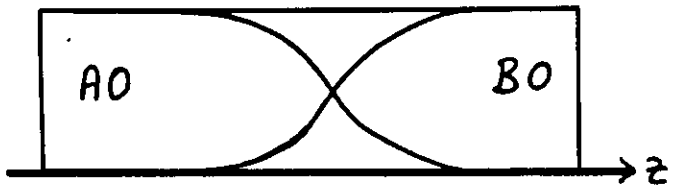
$$ {}_{v}j_A = -\tilde{D} \cdot \nabla c_A = -D \cdot (-\nabla c_B) = -{}_{v}j_B $$

or

$$ {}_{v}j_A + {}_{v}j_B = 0 \qquad (3.73) $$

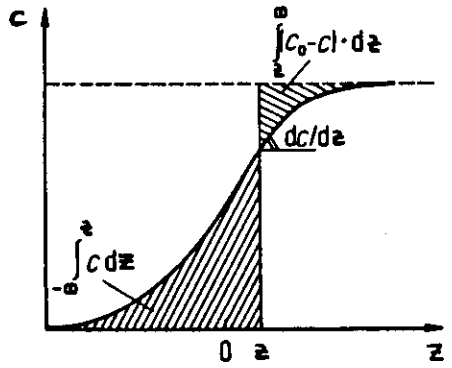
Thus, in the reference which is fixed to a moving surface of the crystal the component fluxes add up to zero, in contrast to the lattice frame.

The measureable interdiffusion profiles of A and B are characterized by a single parameter, the interdiffusion coefficient $\tilde{D}$.



The interdiffusion coefficient, $\tilde{D}$, in (3.72) is strongly dependent on the composition, x. To determine the concentration dependent diffusion coefficient, $\tilde{D}(c)$, experimentally the Boltzmann - Matano analysis is used ($c=x/V_m$):

$$ D(c) = \frac{1}{2 \cdot t \cdot (\partial c/\partial z)} \cdot \left((c_o - c(z)) \cdot \int_{-\infty}^{z} c(z)\, dz + c(z) \cdot \int_{z}^{\infty} (c_o - c(z))\, dz \right) \qquad (3.74) $$



Once a chemical diffusion coefficient, $\tilde{D}(c)$, is determined it can be compared to the Darken relation (3.72), which predicts a value for $\tilde{D}$ with the help of the component diffusion coefficients, D_A and D_B.

3.9 Microscopic diffusion models

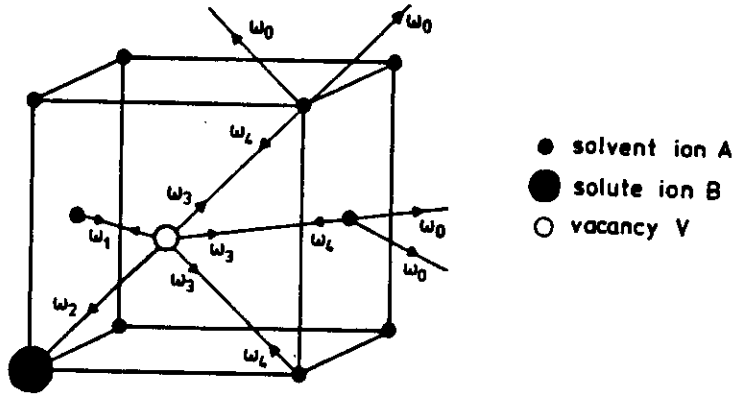
In this last chapter we will discuss two microscopic diffusion models which describe diffusion of two mobile components, A and B, via vacancies. The first model, the five-frequency model, describes diffusion in a dilute solid solution while the second model, the random alloy model, describes diffusion in a concentrated solid solution. Both models were developed for binary alloys, $A_{1-x}B_x$, however they can also be used for ternary compounds, $(A_{1-x}B_x)X$, where the component X is immobile, as this is the case for several oxides or sulfides. It should be emphasized that these two models are the only exact diffusion models for diffusion within a crystalline solid. In both cases it is the aim to calculate the transport parameters which describe diffusion, i.e. the diffusion coefficients, D_i, and the transport coefficients, L_{ij}, as a function of the elementary jump frequencies of the mobile components.

(a) Five - frequency - model

The model (Lidiard, 1956) describes diffusion within a fcc-lattice and in a dilute solid solution, where A is the solvent ion and B is the solute ion, e.g. $(A_{1-x}B_x)O$ with $x<<1$. As usual in vacancy diffusion, the B ions can jump only when they occupy a lattice site adjacent to a vacancy. Due to the fact that the B ions are strongly diluted this arrangement forms a distinguishable pair within the solvent system AO. These pairs, (B,V), can form randomly with a short lifetime

or they can form due to an attractive interaction with a longer lifetime, as this was discussed earlier (see chapter 2.7).

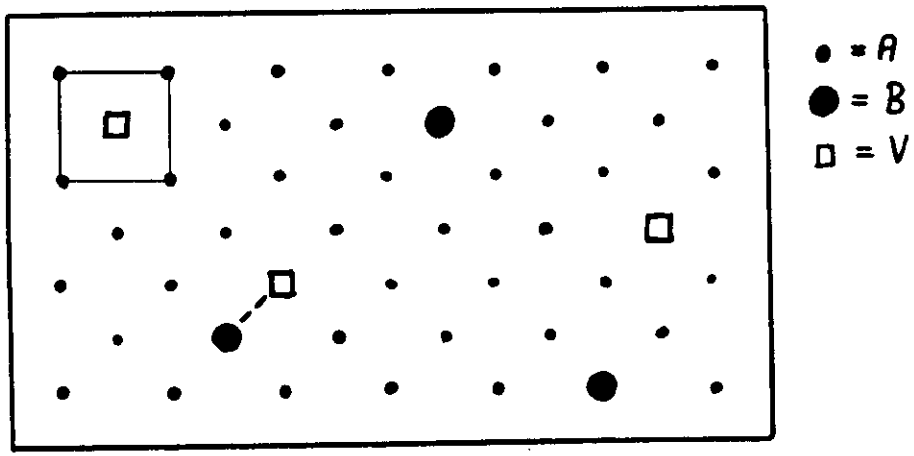
The nature of the model is defined in the next figure where only the cation sites are shown:



In this diagram a single solute - vacancy pair, (B,V), is shown while all other sites are occupied by solvent ions A. Jumps of the vacancy are only allowed to nearest neighbor sites and the jump frequencies of the vacancy to the various sites are indicated by the symbols w_0, w_1, w_2, w_3 and w_4 which have the following meaning.

w_0 = exchange of V and A in the pure crystal AO
w_2 = exchange of V and B
w_1 = exchange of V and A in the nearest neighborhood of the solute B
w_3 = exchange of V and A, dissociative for the pair
w_4 = exchange of V and A, creating a pair

The five - frequency - model is a nearest neighbor model allowing for a specific interaction between the solute, B, and the vacancies, V, which shows up in the different jump frequencies of the vacancy in the surrounding of the solute.



If x_B^* is the overall molar fraction of solute, B, and if x_B^f and x_V^f are the molar fractions of unpaired, i.e. free, solutes and vacancies, then the number of pairs, x_p, can be calculated from the chemical equilibrium

$$B_A + V_A = (B_A,V_A), \qquad K_p = 12 \cdot e^{-\Delta G_p/RT} = \frac{x_p}{x_B^f \cdot x_V^f} \tag{3.75}$$

where 12 is the number of distinct orientations of the pair and ΔG_p is the solute - vacancy binding energy (see chapter 2.7). Due to detailed balance the binding energy determines the ratio of w_4 and w_3:

$$w_4/w_3 = \exp(-\Delta G_p/RT) \tag{3.76}$$

Without going into the details of the derivation the results for the transport parameters in this model are:

The solute diffusion coefficient, D_B, is given by:

$$D_B = (1/6) \cdot a^2 \cdot w_2 \cdot p \cdot f_B \tag{3.77}$$

where $p = x_p/x_B^*$ is the degree of pairing of B and f_B is the physical correlation factor for the motion of B which will be discussed later. This result which is valid for small solute concentrations can be discussed for two limiting cases.

(i) $\Delta G_p = 0$

This limiting case describes diffusion of homovalent solutes, B, in an AO matrix where the solute - vacancy binding is expected to be negligible. Therefore, the jump frequencies w_0, w_1, w_3 and w_4 are identical and only two different frequencies, w_0 and w_2, remain. In this two- frequency model pairs are formed only randomly and the number of pairs is:

$$x_p = 12 \cdot x_B \cdot x_V, \qquad p = 12 \cdot x_V \tag{3.78}$$

resulting in a solute diffusion coefficient

$$D_B = 2 \cdot a^2 \cdot w_2 \cdot x_V \cdot f_B \tag{3.79}$$

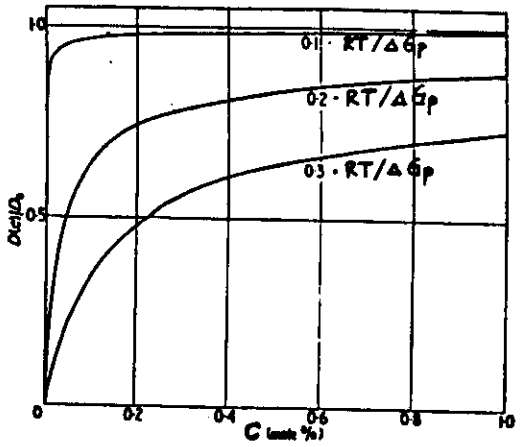
This results looks very similar to the result for the tracer diffusion coefficient found in chapter 3.3. The diffusion coefficient is proportional to a geometric factor, to the jump frequency, w_2, and to the number of vacant lattice sites, x_V. The physical correlation factor, f_B, describes the correlated walk of the solute which is due to the different exchange frequencies of a vacancy with A and with B.

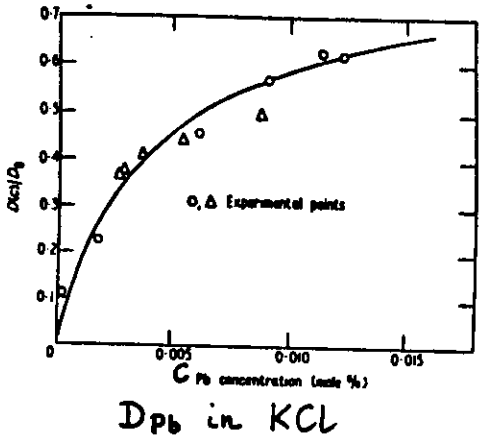
$$f_B = \frac{w_0}{w_0 + (1/f-1)\cdot w_2} \qquad (3.80)$$

Here f=0.781 is the geometrical correlation factor for diffusion via vacancies in a fcc-lattice. The correlated walk of the solute can be understood as follows. If $w_2 = w_0$, then $f_B = f$, i.e. the solute B behaves like a tracer of the solvent A. If $w_2 >> w_0$, then the probability is large that the ion B, after exchanging sites with a vacancy, immediately jumps back into the vacancy. Although B jumps fast compared to A its mean square displacement is small, resulting in a small correlation factor, $f_B = w_0/(1/f-1)\cdot w_2) << 1$. Finally, if $w_2 << w_0$, then B moves uncorrelated, $f_B = 1$.

(ii) $\Delta G_p < 0$ and $|\Delta G_p| > RT$

This describes diffusion of solutes with a strong attractive interaction to vacancies, for example the diffusion of Cr^{3+} in NiO. The degree of pairing, p, is a function of the solute concentration, x_B^*, approaching the saturation value 1 for large solute concentrations. Thus, the solute diffusion coefficient, D_B, in (3.77) is a strong function of the solute concentration x_B^*:





D_{Pb} in KCl

Finally, the transport coefficients are known within this diffusion model. For simplicity only proportionalities are given:

$$L_{AA} \sim w_0\cdot x_V^f + F_1(w_0,w_1,w_2,w_3,w_4)\cdot x_p \qquad (3.81)$$

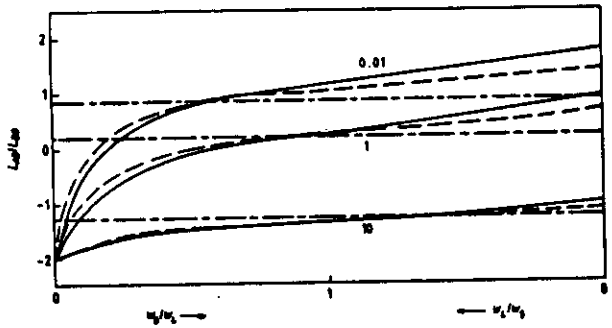
$$L_{AB} \sim F_2(w_0,w_1,w_2,w_3,w_4)\cdot x_p \qquad (3.82)$$

$$L_{BA} = L_{AB} \qquad (3.83)$$

$$L_{BB} \sim F_3(w_0,w_1,w_2,w_3,w_4)\cdot x_p \qquad (3.84)$$

Here F_1, F_2 and F_3 are complicated functions of the jump frequencies w_i. The transport coefficient L_{AA} consists of a simple term which is due to the exchange of A with free vacancies and of a more complicated term which describes the

possibility of exchange between A and vacancy located in a pair. In contrast, L_{BB} describes the motion of B which is only possible within a pair. The cross coefficient, L_{AB}, is also proportional to x_p and can be of the same order of magnitude as L_{BB}. In addition, L_{AB} can be positive or negative, depending on the relative magnitudes of the exchange frequencies w_i.



(b) Random alloy model

The random alloy model (Manning, 1967) describes diffusion in concentrated solid solutions, for example in $(A_{1-x}B_x)O$ with $x \approx 0.5$. The complicated spectrum of jump frequencies belonging to all possible A - B arrangements is approximated by average jump rates. In this way, the jump frequency of the vacancy, Γ_V, in the mixed oxide, (A,B)O, consists of the averaged jump frequencies, $\Gamma_V(A)$ and $\Gamma_V(B)$, in the pure oxides, AO and BO, respectively.

$$\Gamma_V = x_A \cdot \Gamma_V(A) + x_B \cdot \Gamma_V(B) \qquad (3.85)$$

In contrast to the simple binary crystals, AO or BO, where the vacancy jumps are uncorrelated (random walk), now also the vacancy jumps are correlated which is described by a vacancy correlation factor, f_V. Since the jumps of A or B are also correlated (resulting in f_A and f_B) there are now three correlation factors in this model. However, with the help of special kinetic arguments, Manning was able to express the measurable tracer diffusion coefficients, D_A and D_B, in the mixed oxide as a function of the elementary jump frequencies, $\Gamma_V(A)$ and $\Gamma_V(B)$, the molar fraction of vacancies, x_V, and the composition, x. Comparing the results of his kinetic model with linear transport theory he was able to specify relations for the transport coefficients. The result is that the transport coefficients are determined definitely by the tracer diffusion coefficients, D_A and D_B.

$$L_{AA} = \frac{c_A \cdot D_A}{RT} \cdot \left(1 + \frac{2 \cdot c_A \cdot D_A}{M_0 \cdot (c_A \cdot D_A + c_B \cdot D_B)} \right) \qquad (3.86)$$

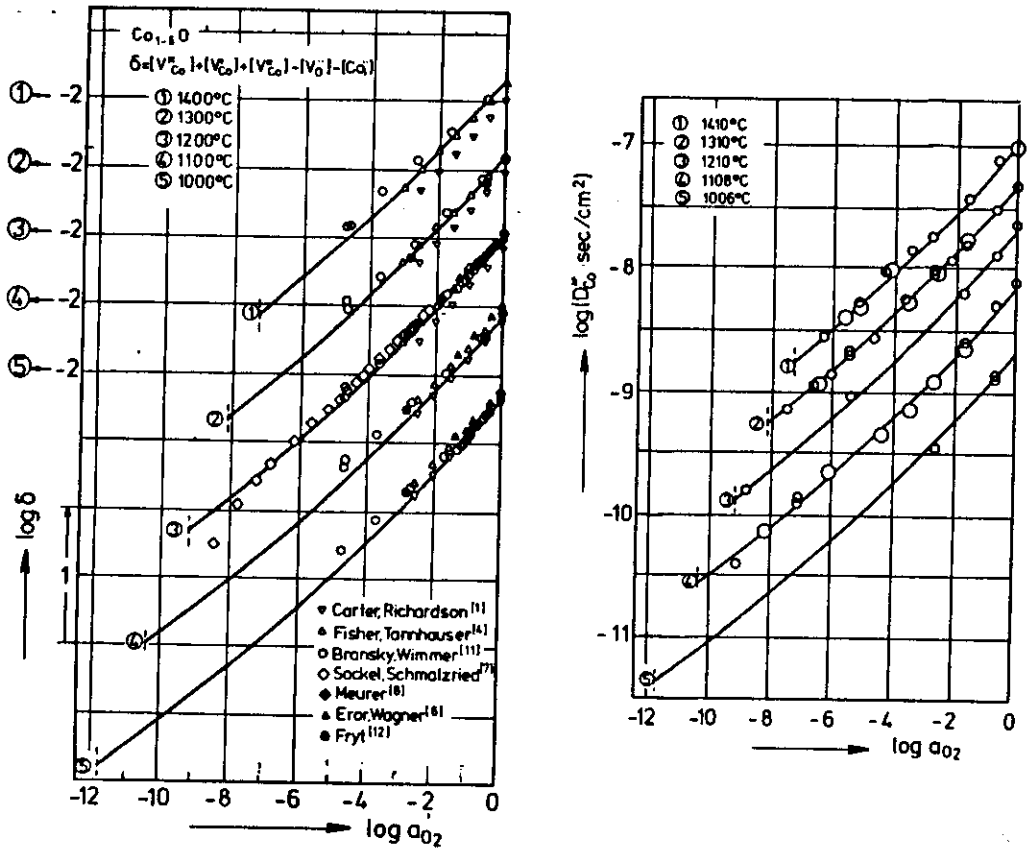
$$L_{AB} = \frac{2}{M_0 \cdot RT} \cdot \frac{c_A \cdot D_A \cdot c_B \cdot D_B}{c_A \cdot D_A + c_B \cdot D_B} = L_{BA} \qquad (3.87)$$

$$L_{BB} = \frac{c_B \cdot D_B}{RT} \cdot \left(1 + \frac{2 \cdot c_A \cdot D_A}{M_0 \cdot (c_A \cdot D_A + c_B \cdot D_B)} \right) \qquad (3.88)$$

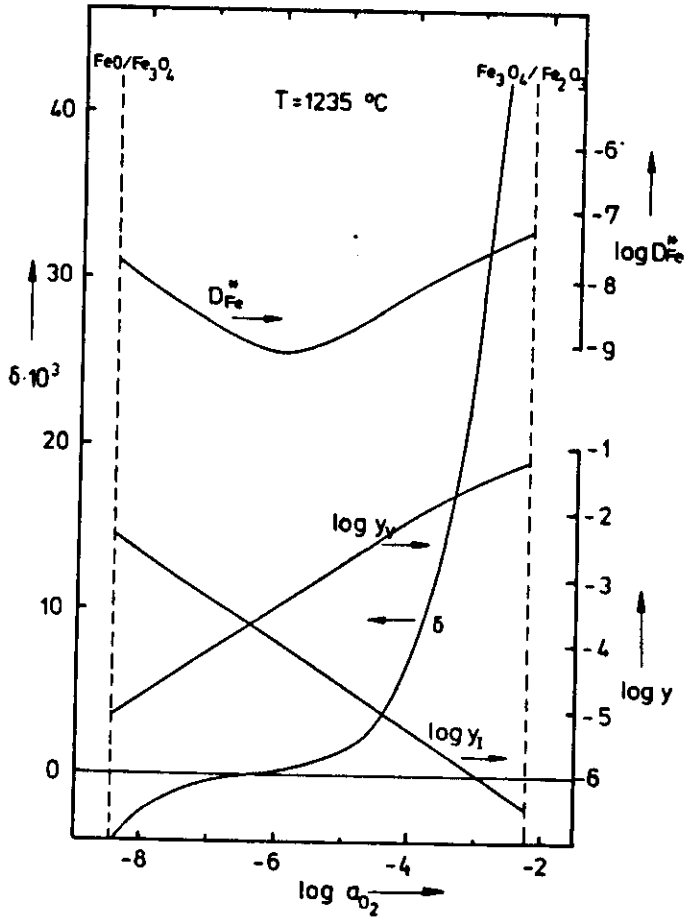
where M_0 is a constant determined by the lattice structure. Like in the five - frequency model, Onsager's reciprocal relation, $L_{AB} = L_{BA}$, appears as a result of the particular model.

3.10 Examples

Example (a): Tracer diffusion in $Co_{1-\delta}O$



Example (b): Tracer diffusion in magnetite (Fe_3O_4)



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