VI. Kinetics of Solids

8. Transport Processes in Solids

8.1. Phenomenological Treatment

Description by macroscopic quantities which may be determined experimentally such as D, \(\sigma\), b or Onsager-coefficients. These quantities will be later related to atomistic processes by statistical considerations.

Average velocity \(v = \frac{s}{t}\) (8.1)
as a result of the force \(F\) which acts upon the species

\[b = \frac{v}{F}\] (8.2)

\[j = cv = cbF\] (8.3)

Driving forces are e.g.:
- Concentration-/Activity gradients
- Electrical Fields
Both processes are often occurring simultaneously: This results in the transport in an electrochemical potential gradient
- Temperature gradients

Transport processes are irreversible phenomena which require the application of irreversible thermodynamics. The forces and fluxes of irreversible thermodynamics have to be chosen such that

\[\sum (\text{Forces} \times \text{Fluxes}) = \text{Entropy production}\]
of the considered process.

Suitable forces for the fluxes of species:

\[\text{grad} (\frac{\eta}{T})\]
(\(J\times\text{grad} (\frac{\eta}{T})\): Ws / K cm\(^3\) s)

Flux of two types of species under isothermal conditions:

\[j_1 = L_{11} \text{grad } \eta_1 + L_{12} \text{grad } \eta_2\] (8.4)

\[j_2 = L_{21} \text{grad } \eta_1 + L_{22} \text{grad } \eta_2\] (8.5)

\(L_{ij}\): Onsager-coefficients

Onsager’s reciprocity relation:

\[L_{ij} = L_{ji}\] (8.6)

If the coupling of fluxes may be neglected:

\[L_{ij} = 0 \text{ for } i \neq j\] (8.7)

\[j_i = L_{ii} \text{grad } \eta_i\] (8.8)

Comparison with \(j_i = -c_i b_i \text{grad } \eta_i\) (8.9)

\[L_{ii} = -c_i b_i\] (8.10)

Fick’s Diffusion

Dynamic Equilibrium:

\[\sum \text{all fluxes} = 0 \text{ (motion of species in all directions)}\]

In the case of the presence of concentration gradients:

Net flux of species = diffusional flux \(j\)

\[j = -DF \frac{\partial c}{\partial x}\] 1st Fick’s Law (8.11)

(empirically observed by Fick in 1855)

\(D_F\): Fick’s Diffusion Coefficient [cm\(^2\) / s]

In general holds:

\[j = -D_F \text{grad } c = -D_F \text{Vc}\] (8.12)
(\(D_F\): Tensor of 2nd type)

Time dependence of the concentration at the position \(x\):

Given by Fick’s 1st law and continuity considerations (i.e. no formation or no consumption of ions, e.g. by dissociation or recombination)

15.10.01
We look at the volume of the slab between $x$ and $x + \Delta x$. $N(x, t)$ species are within this range of the slab of a diameter of 1 cm$^2$.

The time dependence of the concentration is given by the difference of fluxes in and out of the volume

$$\frac{\partial N(x, t)}{\partial t} = j(x, t) - j(x + \Delta x, t)$$  \hspace{1cm} (8.13)

with $c = \frac{N}{\Delta x}$:

$$\frac{\partial c(x, t)}{\partial t} = -\frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right)$$  \hspace{1cm} (8.14)

If $D$ is independent of the concentration, i.e. independent of the position, the following equation holds

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$  \hspace{1cm} (8.15)

(differential equation of 2$^\text{nd}$ order with regard to the space coordinates – two boundary conditions; differential equation of 1$^\text{st}$ order with regard to the time coordinate – one boundary condition)

Solutions of equation (8.16) may be found especially in the books:


The time dependent change of the concentration is proportional to the benditure (2$^\text{nd}$ derivation), i.e. nature shows a tendency to remove strong local variations in the concentration.

Fig. 8.2 At time $t$: $N(x,t)$ species in a tube of 1 cm$^2$ diameter between $x$ and $x + \Delta x$.

Example:

$N_0$ species of a soluble material are located on the surface ($x = 0$; Area = 1 cm$^2$)

Initial conditions:

$$N = N_0 (x = 0, t = 0) \hspace{1cm} (8.17)$$
$$N = 0 \hspace{1cm} (x > 0, t = 0) \hspace{1cm} (8.18)$$

$$\Sigma N = N_0 \Lambda t \hspace{1cm} (8.19)$$

The solution is shown in Fig. 8.3.:

$$N(x,t) = \frac{N_0}{\pi D t} \exp \left( -\frac{x^2}{4Dt} \right)$$  \hspace{1cm} (8.20)

Average distance from the origin

$$\bar{x} = \int_0^\infty \frac{N(x,t)}{N_0} dx$$  \hspace{1cm} (8.21)

is the probability to find one of the $N_0$ species in a layer of thickness $\Delta x$.

$$\bar{x} = \frac{1}{\pi D t} \int_0^\infty \exp \left( -\frac{x^2}{4Dt} \right) dx = 2 \sqrt{\frac{D t}{\pi}} \approx \sqrt{Dt}$$  \hspace{1cm} (8.22)

Number of species which remain within the average distance $\bar{x}$:

$$N(x \leq \bar{x}, t) = \int_0^{\bar{x}} N(x,t) dx = 0.68 N_0$$  \hspace{1cm} (8.23)

Mean square of displacement:

$$\sqrt{\bar{x}^2} = \sqrt{\int_0^{\bar{x}} x^2 \frac{N(x,t)}{N_0} dx} = \sqrt{2Dt}$$  \hspace{1cm} (8.24)

Statistical Treatment:

Mean square displacement = sum of individual jumps during the period of time $t$ (Figs. 8.4. and 8.5.):

$$\bar{R} = \sum \bar{r}_i$$  \hspace{1cm} (8.25)
\[ R_2^2(t) = nr^2 \]  
\[ \text{(8.31)} \]

Comparison with \( x^2(t) = 2Dt \):

\[ D = \frac{1}{2} \frac{n}{t} r^2 = \frac{1}{2} \nu r^2 \]  
\[ \text{(8.32)} \]

3-dim.: \[ D = \frac{1}{6} \nu r^2 \]  
\[ \text{(8.33)} \]

If the jumps are not independent of each other

\[ \cos \alpha_{ij} \neq 0 \]  
\[ \text{(8.34)} \]

\[ R_2^2(t) = fn r^2 \]  
\[ \text{(8.35)} \]

\[ D = \frac{1}{2} f \nu r^2 \]  
\[ \text{(8.36)} \]

\( f \): Correlation factor:

(\text{dependent on crystal structure and mechanism, Table 8.1.})

Table 8.1. Correlation factor \( f \), in dependence of the mechanism and crystal structure.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Structure</th>
<th>( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>Diamond</td>
<td>0,5</td>
</tr>
<tr>
<td>V</td>
<td>simple cubic</td>
<td>0,653</td>
</tr>
<tr>
<td>V</td>
<td>space centered cubic</td>
<td>0,727</td>
</tr>
<tr>
<td>V</td>
<td>hexag. dense packed</td>
<td>0,781</td>
</tr>
<tr>
<td>V</td>
<td>face centered cubic</td>
<td>0,781</td>
</tr>
<tr>
<td>i</td>
<td>AgCl</td>
<td>1</td>
</tr>
<tr>
<td>indirect i</td>
<td>AgCl</td>
<td>0,33</td>
</tr>
<tr>
<td>- collinear</td>
<td>AgCl</td>
<td>0,727</td>
</tr>
<tr>
<td>- non-collinear</td>
<td>AgCl</td>
<td>0,527</td>
</tr>
</tbody>
</table>

\[ F = - \text{grad} \eta (\mu) \]  
\[ \text{(8.37)} \]

The force results in an average velocity \( v \):

\[ v = b F \]  
\[ \text{(8.38)} \]

\( b \): general mobility

Accordingly, the particle flux \( j \) is given by

\[ j = c v = - c b \text{ grad} \eta \]  
\[ \text{(8.39)} \]
Ideal behavior; neutral species:
\[
\eta = \mu = \mu^0 + kT \ln \frac{c}{c_0} \quad (8.40)
\]
\[
j = -c b kT \frac{d \ln c}{dx} = -b kT \frac{d c}{d x} \quad (8.41)
\]
Coefficient comparison with Fick’s 1st law:
\[
D_F = D = b kT \quad (8.42)
\]
(Nernst-Einstein-Relation)

Non-ideal behavior; neutral species:
\[
\eta = \mu = \mu^0 + kT \ln a \quad (8.43)
\]
\[
j = -c b kT \frac{d \ln a}{dx} = -b kT \frac{d ln a \ de c}{d \ ln c \ dx} \quad (8.44)
\]
\[
j = -D \frac{d \ln a \ de c}{d \ ln c \ dx} \quad (8.45)
\]

D: "Diffusivity" (describes the mobility in the crystal lattice – without directed driving forces)
\[
\frac{d \ln a}{d \ln c} = \text{Wagner factor} \quad (8.46)
\]
\[
D_F = D = \frac{d \ln a}{d \ln c} \quad (8.47)
\]

Tracer diffusion (Self diffusion)
\[
\text{Diffusion of a radioactive isotope in electrochemical equilibrium}
\]
\[
D_T = \text{f} b kT = fD \quad (8.48)
\]
(f: correlation factor)

Charged species in an electrical field
If there is no concentration gradient, the flux is given by
\[
j = -c b z q \text{ grad } \varphi \quad (8.49)
\]

Comparison with Ohm’s law (which holds at sufficiently low electrical fields, i.e. as long as the product of the electrostatic potential difference per lattice distance multiplied by the elemental charge if small compared to \(< kT)\),
\[
i = -\sigma \text{ grad } \varphi \quad (8.50)
\]
\[
\sigma = \sum_i \sigma_i \quad (8.51)
\]
and under consideration of
\[
i = z q j \quad (8.52)
\]
\[
\sigma = c b z^2 q^2 \quad (8.53)
\]
\[
c [\text{species / cm}^3] \quad (8.54)
\]

Electrical mobility \(u\):
\[
|v| = u |\text{grad } \varphi| \quad (8.55)
\]

Force upon a charged species in an electrical field:
\[
F = -z q \text{ grad } \varphi \quad (8.56)
\]
\[
|v| = b q |z \text{ grad } \varphi| \quad (8.57)
\]

Comparison:
\[
u = |z| q b \quad (8.58)
\]

Description of the particle fluxes in the general case of chemical potential and electrostatic potential gradients by \(b, u, D\) and \(\sigma\):
\[
j = -c b \text{ grad } \eta \quad (8.59)
\]
\[
\text{grad } \eta = \text{grad } \mu + z q \text{ grad } \varphi \quad (8.60)
\]
\[
= -\frac{c u}{|z| q} \text{ grad } \eta \quad (8.61)
\]
\[
= -\frac{c D}{kT} \text{ grad } \eta \quad (8.62)
\]
\[
= -\frac{\sigma}{z^2 q^2} \text{ grad } \eta \quad (8.63)
\]

8.2.3. Chemical Diffusion

Electroneutrality:
\[
\sum_i z_i j_i = 0 \quad (8.64)
\]
In general interaction between the two fastest species. The second fastest species are rate determining.
\[
z_i j_1 = -z_2 j_2 \quad (8.65)
\]
\[
J_i = -D_i \frac{\partial c_i}{\partial x} \quad i = 1, 2 \quad (8.66)
\]
\[ \partial c_1 / \partial x = -z_2 \partial c_2 / \partial x \] (8.67)

In view of \( z_1 c_1 = -z_2 c_2 \) we have

\[ \beta_1 \beta_2 \cdot \beta = \beta \] (8.69)

Feeding

\[ j_i = -kT u_i q \left[ \frac{\partial \ln a_i}{\partial \ln c_i} + \frac{z_i q c_i}{kT} \right] \] (8.70)

into the electroneutrality condition, resolving the equation for \( \partial \phi / \partial x \) and elimination of \( \phi / dx \) results in the following flux equation:

\[ j_i = -D \left[ \frac{\partial \ln a_i}{\partial \ln c_i} - \sum_{j=e,h} t_j \frac{z_i}{z_j} \frac{\partial \ln a_j}{\partial \ln c_i} \right] \frac{\partial c_i}{\partial x} \] (8.71)

In view of the ionization equilibrium

\[ d \ln a_i + z_i d \ln c_e = d \ln a_i - z_i d \ln a_h = d \ln a_i \] (8.72)

this results in

\[ j_i = -D \left[ \frac{\partial \ln a_i}{\partial \ln c_i} - \sum_{j=e,h} z_j \frac{\partial \ln a_j}{\partial \ln c_i} \right] \frac{\partial c_i}{\partial x} \] (8.73)

Comparison with \( j_i = -\beta D_i \frac{\partial c_i}{\partial x} \) provides

\[ \beta = D_i W \] (8.75)

\[ W = \left[ (1 - t_i) \frac{\partial \ln a_i}{\partial \ln c_i} - \sum_{j=e,h} t_j z_j \frac{\partial \ln a_j}{\partial \ln c_j} \right] \] (8.76)

### Table 8.2 Wagner factor under general and some special conditions

<table>
<thead>
<tr>
<th>Thermodynamic assumptions</th>
<th>Concentration assumptions</th>
<th>Transference no. assumption</th>
<th>Enhancement factor ((W))</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. General</td>
<td>General</td>
<td>General</td>
<td>[ \frac{\partial \ln a_i}{\partial \ln c_i} + z_i \frac{\partial \ln a_e}{\partial \ln c_e} ] or [ \frac{\partial \ln a_i}{\partial \ln c_i} ]</td>
</tr>
<tr>
<td>b. General</td>
<td>General</td>
<td>( t_i \ll 1 )</td>
<td>[ \frac{\partial \ln a_i}{\partial \ln c_i} + z_i \frac{\partial \ln a_e}{\partial \ln c_e} ]</td>
</tr>
<tr>
<td>c. ( [a_i = (\text{const.}) c_i ]</td>
<td>General</td>
<td>General</td>
<td>[ \frac{\partial \ln a_i}{\partial \ln c_i} + z_i \frac{\partial \ln a_e}{\partial \ln c_e} ]</td>
</tr>
<tr>
<td>d. ( [a_i = (\text{const.}) c_i ]</td>
<td>General</td>
<td>( c_i \ll c_e )</td>
<td>[ \frac{\partial \ln a_i}{\partial \ln c_i} + z_i \frac{\partial \ln a_e}{\partial \ln c_e} ]</td>
</tr>
<tr>
<td>e. ( [a_i = (\text{const.}) c_i ]</td>
<td>General</td>
<td>( t_i \ll 1 )</td>
<td>[ \frac{\partial \ln a_i}{\partial \ln c_i} + z_i \frac{\partial \ln a_e}{\partial \ln c_e} ]</td>
</tr>
<tr>
<td>f. ( [a_i = (\text{const.}) c_i ]</td>
<td>( z_i \ll c_e )</td>
<td>( t_i \ll 1 )</td>
<td>[ \frac{\partial \ln a_i}{\partial \ln c_i} + z_i \frac{\partial \ln a_e}{\partial \ln c_e} ]</td>
</tr>
<tr>
<td>g. ( [a_i = (\text{const.}) c_i ]</td>
<td>( c_i \gg c_e )</td>
<td>( t_i \ll 1 )</td>
<td>[ \frac{\partial \ln a_i}{\partial \ln c_i} + z_i \frac{\partial \ln a_e}{\partial \ln c_e} ]</td>
</tr>
<tr>
<td>h. ( [\text{ion general} ]</td>
<td>General</td>
<td>( t_i \ll 1 )</td>
<td>[ \frac{\partial \ln a_i}{\partial \ln c_i} + z_i \frac{\partial \ln a_e}{\partial \ln c_e} ]</td>
</tr>
</tbody>
</table>
\[
W = t_c \left[ \frac{\partial \ln a_i}{\partial \ln c_i} + z_i \frac{\partial \ln a_e}{\partial \ln c_i} \right] + z_i \frac{\partial \ln a_e}{\partial \ln c_i} \left[ \frac{\partial \ln c_e}{\partial \ln c_i} \right] \tag{8.77}
\]

\[\gamma_i, \gamma_e \approx \text{const (Henry's- or Raoult's law)}\]

\[
W = t_e \left[ 1 + z_i \frac{\partial \ln c_e}{\partial \ln c_i} \right] \tag{8.78}
\]

Electroneutrality condition:

\[
dc_e = z_i dc_i \tag{8.79}
\]

\[
W = te \left[ 1 + z_i^2 \frac{c_i}{c_e} \right] \tag{8.80}
\]

\[
t_e = \frac{\sigma_e}{\sigma_e + \sigma_i} = \frac{c_e D_e}{c_e D_e + z_i^2 c_i D_i} \tag{8.81}
\]

Fig. 8.7 Logarithm of the ratio of the mobilities of electrons and ions against the logarithm of the ratio of the concentrations of electrons and ions. The parameters indicate the Wagner factor \(W\).

\[
W = \frac{c_e D_e}{c_e D_e + z_i^2 c_i D_i} + z_i^2 c_i c_e D_e \tag{8.82}
\]

Fig. 8.9 Wagner Factor as a function of the logarithm of the ratios of the concentration of electrons and ions for various transference numbers of the electrons.

Fig. 8.10 Diffusivity, chemical diffusion and Wagner factor of \(\text{Li}_3\text{Bi}\) as a function of stoichiometry at 380 °C.

Abb. 8.11 Electrical potential difference between two locations of three different materials for a given concentration difference. Voltages up to 10 V may be observed in the case of \(\text{Li}_3\text{Sb}\).
9. Solid State Reactions, Corrosion

9.1 Tarnishing Larger Formation

<table>
<thead>
<tr>
<th>Metal</th>
<th>Tarnishing Layer</th>
<th>oxidant, e.g. O₂, S, Halogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(compact or porous or unregular, e.g. as whisker)</td>
<td></td>
</tr>
</tbody>
</table>

Compact tarnishing layer:

- Cations
- Anions
- Electrons

Partial Reaction Steps:
- a) Transfer of Me through the interface metal \(\mid\) tarnishing layer
- b) Diffusion in the tarnishing layer
- c) Incorporation of the oxidant

Time dependence of the reaction:
- a) Linear relationship
  \[
  \Delta x = \text{const} \cdot t \quad (9.1)
  \]
  \[
  \frac{d}{dt} \Delta x = \text{const} \quad (9.2)
  \]
  holds, if one (or several) of the phase boundary reactions are rate-determining.

Examples:
- i) Oxidation of Fe in CO₂-CO-mixtures at 900 °C.
  Dissociation of CO\(_2\)\(_{\text{ad}}\) in CO\(_{\text{ad}}\) and O\(_{\text{ad}}\) is rate determining.
- ii) Ag + liquid S (at the beginning)
  Transfer of Ag through the phase boundary is rate determining.

b) Parabolic Law

\[
\frac{d}{dt} \Delta x = \frac{k}{\Delta x} \quad (9.3)
\]

\[
\Delta x^2 = 2kT \quad (9.4)
\]

c) Logarithmic Law

\[
\Delta x = a + b \log t \quad (9.5)
\]

(is sometimes observed in the case of small layer thicknesses)

Calculation of \(k\) (parabolic time law)
(C. Wagner, 1933)

Assumptions:
- a) Pore free tarnishing layer
- b) Equilibrium tarnishing layer \(\mid\) adjacent phases
c) Local thermodynamic equilibrium (electrons, ions)
d) Negligible solubility of the oxidant in the metal
e) $\Delta x >>$ thickness of the electrical double layers

Cations: $j_M = -\frac{\sigma_M}{z_M^2 q^2} \frac{\partial n_M}{\partial x} = -\frac{c_M D_M}{kT} \frac{\partial n_M}{\partial x}$ (9.6)

Anions: $j_X = -\frac{\sigma_X}{z_X^2 q^2} \frac{\partial n_X}{\partial x} = -\frac{c_X D_X}{kT} \frac{\partial n_X}{\partial x}$ (9.7)

Electrons: $j_e = -\frac{\sigma_e}{q^2} \frac{\partial n_e}{\partial x} = -\frac{c_e D_e}{kT} \frac{\partial n_e}{\partial x}$ (9.8)

In most cases holds: electrons are the fastest or the second fastest species (process is determined by the motion of cations or anions and electrons).

Assumption: $\sigma_M >> \sigma_X$ (The reverse situation is analogous)

$$z_M j_M = j_e$$ (9.9)

Elimination of the electrical field

$$j_M = -\frac{1}{z_M^2 q^2} \frac{\sigma_M \sigma_e}{\sigma_M + \sigma_e} \left( \frac{\partial \mu_M}{\partial x} + z_M \frac{\partial \mu_e}{\partial x} \right)$$ (9.10)

Integration:

$$j_M = -\frac{1}{z_M^2 q^2} \frac{\sigma_M \sigma_e}{\sigma_M + \sigma_e} \int_{\mu_0}^{\mu} \frac{\sigma_M}{\sigma_M + \sigma_e} d\mu_M.$$ (9.12)

On the other hand side holds:

$$j_M = c_M \frac{d \Delta x}{d t} = k \frac{\Delta x}{\Delta x}$$ (9.13)

and

$$j_M = -\frac{\partial \mu}{\partial x} \frac{d c_M}{d x}$$ (9.14)

Comparison of eqns. (9.13) and (9.14):

$$\frac{d \Delta x}{d t} = \frac{\partial \mu}{\partial x} \frac{d c_M}{d x}$$

$$\frac{d \Delta x}{d t} = D_M t_e \frac{\partial \ln a_M}{\partial \ln c_M}$$

$$k = \frac{1}{c_M} \int_0^L \left( \frac{\partial \mu}{\partial x} \right) d c_M$$

Comparison of eqns. (9.12) and (9.13) results in

$$k = -\frac{1}{z_M^2 q^2 c_M} \frac{\mu_0}{\mu} \int_{\mu_0}^{\mu} \frac{\sigma_M \sigma_e}{\sigma_M + \sigma_e} d\mu_M.$$ (9.10)

In case that $\sigma_e >> \sigma_M$ (predominantly electronically conducting tarnishing layer)

$$k = -\frac{1}{z_M^2 q^2 c_M} \frac{\mu_0}{\mu} \int_{\mu_0}^{\mu} \frac{\sigma_M}{\sigma_M + \sigma_e} d\mu_M.$$ (9.11)

In case of $\sigma_M >> \sigma_e$ (predominantly ionically conducting tarnishing layer)

$$k = -\frac{1}{z_M^2 q^2 c_M} \frac{\mu_0}{\mu} \int_{\mu_0}^{\mu} \frac{\sigma_e}{\sigma_M + \sigma_e} d\mu_M = -\frac{d_e}{z_M^2 kT c_M} \int_{\mu_0}^{\mu} \frac{\mu_0}{\mu} d\mu_M.$$ (9.12)

Examples

a) Cu | Cu$_2$O | PO$_2$ (1000 °C)

Experimental observation:

$\sigma_h \approx pO_2^{1/7}$ (theor. $\approx pO_2^{1/8}$)

Since $c_h \approx \left[ V_{\text{Cu}} \right]$

$$\sigma_{V_{\text{Cu}}} \approx pO_2^{1/7}$$

$$\sigma_{\text{Cu}} \approx \sigma_{\text{Cu}} \left( \frac{pO_2}{pO_2} \right)$$ (9.23)
\[ \sigma_e >> \sigma_{\text{Cu}} : \]

\[ k = -\frac{1}{q^2 c_M} \int_{\mu_{\text{Cu}}}^{\mu_{\text{Cu}}'} \sigma_{\text{Cu}} \, d\mu_{\text{Cu}} \quad (9.24) \]

Gibbs-Duhem relationship: \[ d\mu_{\text{Cu}} = -\frac{1}{2} d\mu_{\text{O}_2} \]

\[ k = -\frac{kT}{4 q^2 c_{\text{Cu}}} \left( \frac{p_{\text{O}_2}'}{p_{\text{O}_2}} \right)^{1/7} \left( \frac{\frac{\sigma_{\text{Cu}}}{\mu_{\text{Cu}}}}{\frac{\sigma_{\text{Cu}}'}{\mu_{\text{Cu}}}'} \right)^{1/7} \quad (9.25) \]

\[ = \frac{7}{4} \frac{kT}{q^2 c_{\text{Cu}}} \left( \frac{\sigma_{\text{Cu}}}{\mu_{\text{Cu}}} \right)^{1/7} \left( \frac{p_{\text{O}_2}'}{p_{\text{O}_2}} \right)^{1/7} - 1 \quad (9.26) \]

This expression has been experimentally confirmed!

b) Zn | ZnO | p_{\text{O}_2} (400 °C)

\[ \sigma_{\text{Zn}} = \sigma_{\text{Zn}}' \left( \frac{p_{\text{O}_2}'}{p_{\text{O}_2}} \right)^{-1/4} \quad (9.27) \]

\[ k = \text{const} \left[ 1 - \left( \frac{p_{\text{O}_2}}{p_{\text{O}_2}'} \right)^{1/7} \right] \quad (9.28) \]

c) Ag | Ag_2S | S_{\text{liq.}} (400 °C)

\[ \sigma_{\text{Ag}} \approx \text{const} \quad \text{(independant of } a_{\text{Ag}}) = 5.5 \, \Omega^{-1} \, \text{cm}^{-1} (400 °C) \]

\[ k = \frac{\sigma_{\text{Ag}}}{q^2 c_{\text{Ag}}} \left( \mu_{\text{Ag}} - \mu_{\text{Ag}'} \right) \quad (9.29) \]

d) \[ \mu_{\text{Li}} | \text{Li}_3\text{Sb} | \mu_{\text{Li}'} \]

(Fig. 9.1 and 9.2)

e) Formation of double salts:

\[ \text{Ag I} | \text{Ag}_2\text{Hg I}_4 | \text{Hg I}_2 \]

\[ \rightarrow \quad \text{Hg}^{2+} \quad \text{Ag} \]

Parabolic Law:
15.10.01

Increase in the Gibbs energy $\Delta G_1$ by the increase in vacancy concentration from $c_0$ to $c_0 + \Delta c$:

$$\Delta G_1 = n kT \ln \left( \frac{c_0 + \Delta c}{c_0} \right) \approx n kT \frac{\Delta c}{c_0} \left( \Delta c \ll c_0 \right)$$

(9.32)

Simultaneously, the Gibbs energy decreases by the decrease in $\gamma / \rho$ over the sintering areas.

$$\Delta G_2 = n \delta^3 \left( \frac{\gamma}{\rho} \right)$$

($\gamma$: surface energy, $\delta$: atomic distance)

Equilibrium:

$$\Delta G_1 = \Delta G_2$$

(9.33)

$$\Delta c = \frac{\delta^3 \gamma}{\rho} \frac{1}{kT} c_0$$

(9.34)

Time dependence of the broadening of the sintering area:

$$\frac{dx}{dt} = \frac{80}{3} \frac{\delta^3 \gamma a^2}{kT X^3} D$$

(9.35)

9.3. Kirkendall Effect

A binary system (A, B) is considered. Because of different mobilities ($b_A \neq b_B$), the fluxes A and B in opposite directions will not be equal. If there is a local production (or annihilation) of lattice positions, differences in the two fluxes may be compensated by local displacement of the lattice at a velocity $\nu_L$. Then, the following equations for the fluxes hold:

$$j_A = -c_A b_A \nabla \mu_A + c_A \nu_L$$

(9.36)

$$j_B = -c_B b_B \nabla \mu_B + c_B \nu_L$$

(9.37)

For an external observer holds

$$j_A + j_B = 0$$

(9.38)

This condition and Gibbs-Duhem’s relationship results in

$$\nu_L = (b_A - b_B) N_A \nabla \mu_A = (b_B - b_A) N_B \nabla \mu_B$$

(9.39)

The flux $J = j_A - j_B$ is then given by

$$j = c_i (N_B B_A + N_A B_B \nabla \mu_i) \quad (i = A, B)$$

(9.40)

Under the assumption of a vacancy mechanism, the vacancies will generate the local lattice velocity

$$\nu_L = j_v \cdot v_m$$

(9.41)

Equation (9.39) may be then rewritten as

$$j_v = c_A (b_A - b_B) \nabla \mu_A = c_B (b_B - b_A) \nabla \mu_B$$

(9.42)

For the observation of the Kirkendall effect, inert markers are inserted at the interdiffusion zone. The production (annihilation-) rate $r_v$ of the vacancies is given by

$$\nabla j_v + r_v = 0$$

(9.43)

($\text{2nd}$ Fick’s law). By feeding eq. (9.39) into equation (9.43), the production rate of vacancies is given by

$$r_v = -\nabla \left( (b_A - b_B) kT W \nabla c_i \right) \approx (b_A - b_B) kT W W^2 c_i$$

(9.44)

The displacement of the inert markers is described by $V_{UL}$. Within and in the vicinity of the interdiffusion zone, pores and changes in the sample geometry have been observed.

For the atomic motion in the case of a Kirkendall effect, a vacancy mechanism is required.
9.4. Partial Conductivities
Assumption: $\sigma_e << \sigma_i$.

By application of ideal reversible electrodes, Ohm’s law holds (2-pole-technique).

Frequently, electrodes are polarizable. In this case, separate voltage-probes have to be used (i.e. electronic leads in the distance $L$ (4-point-technique):

$$\sigma = \left( \frac{i}{E} \right) L$$

Determination of the identity of the mobile charge carriers and determination of the transference numbers:

Transference measurements:

$$\frac{\Delta m}{\Delta t} = \frac{A}{z} \cdot F$$

(Farraday’s law). $A =$ atomic weight of the transferred charge carrier; $z =$ charge number.

Impedance measurement ("Impedance spectroscopy")

Application of alternating current of small amplitudes in the frequency range between about $10^{-5} - 10^{+5}$ Hz with the determination of the phase shift of the current versus voltage and the ratio of the voltage versus current.

Determination of the total resistance:

$$\sigma_p << \sigma_s :$$

$$R_{ges} = \frac{1}{1 + \frac{R}{w} \left( \frac{1}{c_p} + \frac{1}{c_s} \right)^2 + R^2 w^2 c_p^2 c_s^2}$$

$$W$$ very large ($W >> 1 / R c_p$):

$$R_{ges} = \frac{\frac{1}{R w^2 c_p^2} - i \frac{1}{w c_p}}{1 + \frac{R^2}{w^3 c_p} \frac{w^2}{c_p}}$$

$$W$$ small ($W << \frac{1}{R \sqrt{c_s c_p}}$):

$$R_{ges} = R - i \frac{1}{w c_s}$$
9.5 Current-Voltage Curve for mixed ionic and electronic conducting solids between a reversibe electrode (for defined stoichiometry) and an inert electrode.

Arrangement (Polarisation Measurement):

Reversible electrode | mixed conductor | inert electrode
\[ \downarrow \]
(e.g. Ag for Ag\textsuperscript{+}-ionic conductor, or O\textsubscript{2} for O\textsuperscript{−}-ionic conductor.)

Def.: i \( \equiv \) Ion (mobile ionic species)
e \( \equiv \) electron (excess electron)
h \( \equiv \) hole (defect electron)

Generally holds for the flux density of species in an electrical field and a concentration gradient

\[ j = - \frac{\sigma}{z^2 q^2} \frac{dn}{dx} = - \frac{\sigma}{z^2 q^2} \left( \frac{d\mu_i}{dx} + zq \frac{d\phi}{dx} \right) \] (9.51)

In steady state holds for the flux of ions i:

\[ j_i = 0 \] (9.52)

since the applied voltage is polarized in such a way that no supply of ions by the inert (blocking) electrode is possible.

As a consequence of equations (9.51) and (9.52)):

\[ \frac{d\phi}{dx} = - \frac{1}{z_i q} \frac{d\mu_i}{dx} \] (9.53)

Then according to equation (9.51) holds under consideration of equation (9.53) (for the electrical field) for the electrical current density \( i = zqj \) for the electrons e and holds h

\[ i_{e,h} = - \frac{\sigma_{e,h}}{z_{e,h} q} \left( \frac{d\mu_{e,h}}{dx} - z_{e,h} q \frac{d\mu_i}{dx} \right) \] (9.54)

a) \( d\mu_i >> d\mu_e \) (metallic conductor)

\[ i_{e,h} = + \frac{\sigma_{e,h}}{z_i q} \frac{d\mu_i}{dx} \] (9.55)

or according to equation (9.53)

\[ i_{e,h} = - \sigma_{e,h} \frac{d\phi}{dx} \] (Ohm’s law) (9.56)

b) \( d\mu_e >> d\mu_i \) (semiconductor; ionic conductor)

Equation (9.53):

\[ \frac{d\phi}{dx} = 0 \]

The solid material is free of an electrical field!

\[ i_{e,h} = - \frac{\sigma_{e,h}}{z_{e,h} q} \frac{d\mu_{e,h}}{dx} \] (9.57)

The current is passed by diffusion!

Integration between the two bordres ' and " :

\[ i_{e,h} L = - \frac{1}{z_{e,h} q} \int_{'}^{''} \sigma_{e,h} d\mu_{e,h} \] (9.58)
(L = length, thickness of the sample)

Because of \( \sigma_{e,h} = c_{e,h} \), \( u_{e,h} \), \( q \) holds under the assumption of ideal behavior \((\mu = \mu^0 + kT \ln c)\)

\[
\sigma_{e,h} = \sigma_{e,h} \exp \left( \frac{\mu_{e,h} - \mu_{e,h}^0}{kT} \right) \quad (9.59)
\]

and according equation (9.58) and under consideration of \( E = \frac{1}{a} \left( \mu_{e} - \mu_{e}^{0} \right) \):

\[
i_{e,h} L = \frac{kT}{q} \left[ \sigma_{e} \left( \frac{qE}{kT} - 1 \right) + \sigma_{h} \left( 1 - e^{-\frac{qE}{kT}} \right) \right] \quad (9.60)
\]

\[
i_{\text{ion}} + i_{e} = 0 \quad (9.61)
\]

\[
\frac{\sigma_{\text{ion}}}{z_{\text{ion}}} \frac{\partial \eta_{\text{ion}}}{\partial x} + \frac{\sigma_{e}}{(-1) q} \frac{\partial \eta_{e}}{\partial x} = 0 \quad (9.62)
\]

Because of \( \eta_{\text{ion}} + z \eta_{e} = \mu_{\text{ion}} \), and by integration over the length of the electrolyte holds

\[
E = \frac{1}{q} \left( \frac{\mu_{e}}{z} - \mu_{e}^{0} \right) = \frac{1}{zq} \int t_{e} \, d \mu_{\text{ion}}^{x} \quad (9.63)
\]

\[
t_{e} = -\frac{q}{zq} \frac{\partial E}{\partial \mu_{\text{ion}}^{x}} \quad (9.64)
\]

Electronic Mobility

**Voltage-Relaxation-Method:**

Fig. 9.10 Voltage-Relaxation-Method for the determination of the diffusion coefficients or mobilities of electrons and holes within a predominant ionic conducting solid. The various possibilities to determine the diffusion coefficients \( D_{e} \) and \( D_{h} \) from short-term \((t << L^2 / D_{e,h})\) and long term behavior \((t >> L^2 / 10 D_{e,h})\) are listed. \( c_{e,h} \): concentration of electrons and holes; \( q \): elementary charge; \( k \): Boltzmann’s constant; \( T \): absolute temperature

**9.6. Phase Transformations**

Phase transformations are processes which result in large changes of extensive microscopic properties as a result of small variations \((p, T, \mu)\). Some specific properties show singularities at the transition point.

**Fig. 9.11**

a) Heterogeneous reaction \( A + B = AB \),
b) Transformation of \( 1 \text{st} \) order,
c) Transformation of \( 2 \text{nd} \) order

2 possibilities:
1) Clustering: Separation of the components in B regions, which are either rich in A or B
2) Ordering: A and B form homogeneously a well-defined pattern.

Driving force in 1): chemical potential gradient.
In 2) no transport occurs over microscopic distances; ordered domains are formed initially, which then grow and reduce the Gibb’s energy (mostly by changes in the configuration ordering).

Polymorphic transformation: no macroscopic transport during non-diffusive transformation in the case of a heterogeneous process.

Martensitic Transformation: Lattice shifts control the macroscopic changes of the shape of the sample.

Homogeneous phase transformations occur by continuous ordering in one or several sublattices or by correlated displacive movements.

If the entropy change is 0 ($\Delta S = \partial \Delta G / \partial T$) no transformation of 1st order occurs. Order-disorder transformations are of 2nd or higher order (the 2nd derivative $\partial^2 \Delta G / \partial T^2$ does not disappear).

9.7 Martensitic Transformations

Fig. 9.12: Fast quenching to the 2-phase region $\alpha + \beta$.
The crystal is then supersaturated with regard to component B. Diffusional jumps are frozen in. Some crystals show in this case a diffusionless phase transformation $\beta \rightarrow \beta'$ into another crystal structure: Martensitic Transformation. Martensitic transformations may occur at low temperature ($\approx 100$ K), i.e. if the diffusion is frozen in.

Fig. 9.12: shows an example of $\beta \rightarrow \beta'$-transformation.

Fig. 9.13 Example of a martensitic reaction

The lattice variation from fcc to bcc with 20% contraction along one axis and 20% expansion and 12% expansion along the other two axis.

9.8 Phase Transformation of 2nd order

Phase transformations of 2nd order are diffusionless; however, in contrast to transformations of 1st order (e.g. martensitic transformations), which show a continuous variation in G ($\Delta S \neq 0$), the transformation entropy is 0. The transformation occurs without nucleation and growth of a new phase.

3 types of transformation of 2nd order are distinguished:
1) Order-disorder
2) Displacive
3) Combination of 1) and 2)

Diffusive Transformation

Change in the composition $\alpha \rightarrow \beta$ is very small. The polymorphic transformation is a limiting case with $\gamma = 0$.
Fig. 9.15 Gibb's energy of a binary system with a missibility gap

Fig. 9.15 Gibbs energy as a function of composition

Spinodal Decomposition