Chapter 3: Chemical preparation and crystal growth

3.1 Possible reaction paths of solid state reactions
3.2 Chemical transport reactions
3.3 Crystal refinement by floating zone melting
3.4 Growth of single crystals
3.5 Chemical Vapor Deposition (CVD)
3.6 High pressure syntheses
3.1 Possible reaction paths between two solid grains A and B
3.1 Importance of the surface area for solid state reactions

The *common surface* of reacting grains influences strongly the reaction rate.

Cube: 1 cm edge length
Surface area $S = 6 \text{ cm}^2 = 6 \times 10^{-4} \text{ m}^2$

Grinding

Typical 10 $\mu$m edge length

10 $\mu$m = $10^{-5}$ m $\rightarrow$ $S = 6 \times 10^{-10} \text{ m}^2$

10$^9$ particles $\rightarrow S_{\text{total}} = 6 \times 10^{-1} \text{ m}^2$

Enlargement of the surface area by a factor of $10^3$
3.1 Velocity of diffusion of particles (ions, atoms ...) in a solid

- mass transport and concentration gradient for a given point in a solid!

\[ J_i = -D_i \cdot \frac{\delta c_i}{\delta x} \text{ [mol cm}^{-2}\text{ s}^{-1}] \]

(1st law of Fick)

- \( J_i \): flow of diffusion (mol s\(^{-1}\) cm\(^{-2}\));
- \( D_i \): diffusion coefficient (cm\(^2\) s\(^{-1}\))
- \( \frac{\delta c_i}{\delta x} \): concentration gradient (mol cm\(^{-3}\) cm\(^{-1}\)) (i.e. change of concentration along a line in the solid!)

- Typical diffusion coefficients \( D_i \) for ions (atoms) in a solid at room temperature are about \( 10^{-13} \) cm\(^2\) s\(^{-1}\).
- In solid state ionic conductors (e.g. Ag-ions in \( \alpha \)-AgI) the values are greater by orders of magnitude (\( \approx 10^{-6} \) cm\(^2\) s\(^{-1}\))
3.1 Diffusion coefficients show an exponential temperature dependence (Arrhenius type)

\[ D = D_\infty \exp(-Q/kT) \quad (D_\infty : D \text{ für } T \to \infty, Q: \text{activation energy of diffusion}, k: \text{Boltzmann-faktor}) \]

The logarithmic representation of \(D\) versus \(1/T\) is linear, the slope corresponds to the activation energy and the intercept to \(D_\infty\).
3.1 Model for a classical solid-solid reaction (below melting point!):
Planar interface between two crystals

Assumed: single crystals and volume diffusion only (see transparency 1)

\[ \text{MgO} + \text{Al}_2\text{O}_3 \rightarrow \text{MgAl}_2\text{O}_4 \text{ (spinell)} \]
3.1 Gibbs free enthalpy for the first steps of the formation of seeds (nucleation)

\[ \Delta G = \Delta G_s 4\pi r^2 + \Delta G_v 4/3\pi r^3 \]

- \( r \): radius of spheric seed
- \( r^* \): critical radius
  \( (r>r^* \text{ seed grows by itself}) \)

\( \Delta G_s \): surface free energy change
\( \Delta G_v \): volume free energy change
3.1 Container materials for solid state reactions

- depends on the maximum reaction temperature and/or the type of reacting material (e.g. quartz is an „acidic“ solid unsuitable for „basic“ reactands)

<table>
<thead>
<tr>
<th>Type</th>
<th>Materials</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) glasses</td>
<td>PYREX (DURAN): borosilicate glass (76% SiO₂, 16% B₂O₃, BaO...)</td>
<td>T_max. ~ 400 °C</td>
</tr>
<tr>
<td></td>
<td>QUARTZ: Pure amorphous SiO₂</td>
<td>T_max. ~ 1100 °C</td>
</tr>
<tr>
<td>b) ceramics</td>
<td>Al-silicates:</td>
<td>T_max. ~ 1700 °C</td>
</tr>
<tr>
<td></td>
<td>Corundum (α-Al₂O₃):</td>
<td>T_max ~ 1900 °C</td>
</tr>
<tr>
<td></td>
<td>MgO:</td>
<td>T_max ~ 2200 °C</td>
</tr>
<tr>
<td></td>
<td>BN:</td>
<td>~ 2900 °C</td>
</tr>
<tr>
<td>c) metals</td>
<td>Steel:</td>
<td>~ 1400 °C (under inert gas)</td>
</tr>
<tr>
<td></td>
<td>Pt:</td>
<td>~ 1600 °C (PtO↑), Mo:</td>
</tr>
<tr>
<td></td>
<td>Ta:</td>
<td>~ 2500 °C</td>
</tr>
</tbody>
</table>
3.2 Chemical transport reaction

A solid is dissolved in the gas phase at one place (T=T1) by reaction with a transporting agent (e.g. I₂).

At another place (T=T2) the solid is condensed again.

Whether T₁ < T₂ or T₁ > T₂ depends on the thermochemical balance of the reaction!
Transport can proceed from higher to lower or from lower to higher temperature.

trace of a transporting agent (e.g. I₂)
3.2 Transport direction and examples for chemical transport reactions

Transport direction

\[ \text{hot} \rightarrow \text{cold} \quad \text{or} \quad \text{cold} \rightarrow \text{hot} \]

depends on the enthalpy of the transport reaction

\[ A_{(\text{solid})} + B_{(\text{gas})} \leftrightarrow AB_{(\text{gas})} \quad \Delta H = ??? \]

\( \Delta H > 0 \) (endothermic): hot \( \rightarrow \) cold \n\( \Delta H < 0 \) (exothermic): cold \( \rightarrow \) hot

Some examples for transport reactions:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T1/T2 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( W + 3\text{Cl}_2 \leftrightarrow W\text{Cl}_6 )</td>
<td>400/1400 (exo)</td>
</tr>
<tr>
<td>( \text{Ni} + 4\text{CO} \leftrightarrow \text{Ni(CO)}_4 )</td>
<td>50/190 (exo)</td>
</tr>
<tr>
<td>( 2\text{Al} + \text{AlCl}_3 \leftrightarrow 3\text{AlCl} )</td>
<td>1000/600 (endo)</td>
</tr>
<tr>
<td>( 4\text{Al} + \text{Al}_2\text{S}_3 \leftrightarrow 3\text{Al}_2\text{S} )</td>
<td>1000/900 (endo)</td>
</tr>
</tbody>
</table>

Main application: crystallisation and purification of solids
3.2 Estimation of $\Delta H$ for a transport reaction e.g.:

$\text{ZnS}_\text{(s)} + I_2\text{(gas)} \leftrightarrow \text{ZnI}_2\text{(gas)} + S\text{gas}$ \hspace{1cm} $\Delta H = ??$

$\text{Zn}_\text{(s)} + I_2\text{(g)} \leftrightarrow \text{ZnI}_2\text{(gas)} \hspace{1cm} \Delta H = - 88 \text{ kJ mol}^{-1}$

$\text{ZnS}_\text{(s)} \leftrightarrow \text{Zn}_\text{(s)} + S\text{(g)} \hspace{1cm} \Delta H = +201 \text{ kJ mol}^{-1}$

$\sum \text{ZnS}_\text{(s)} + I_2\text{(gas)} \leftrightarrow \text{ZnI}_2\text{(gas)} + S\text{gas} \hspace{1cm} \Delta H = +113 \text{ kJ mol}^{-1}$

transport from hot to cold (normal conditions provided)!

Question: Which informations/corrections are necessary to calculate the enthalpy values for „realistic“ conditions?
3.2 Application of chemical transport: halide lamp!

- $I_2$ as $\text{CH}_3\text{I}$ and traces of $O_2$

**Initial assumption:** "self repair mechanism": $W$ condenses at the hot/thin parts of the filament:

\[ W + \frac{1}{2} O_2 + I_2 \rightarrow WO_2 I_2 \Delta H \text{ exo (I)} \]

However:

\[ WO_2 I_2 \rightarrow WO_2 + I_2 \]
\[ WO_2 \rightarrow WO + \frac{1}{2} O_2 \]

**Final reaction near the filament:**

\[ W_s + \frac{1}{2} O_2 \rightarrow WO_g \Delta H \text{ endo (I)} \]

($W$ condenses at the cold/thick parts of the $W$ filament) sorry!
3.2 A further application of chemical transport: purification of Ti

transport reaction: \( \text{Ti} + 2\text{I}_2 \rightarrow \text{TiI}_4 \)  \( \Delta H = -376 \text{ kJ mol}^{-1} \) (exothermic: transport from \textit{cold to hot})

W-filament (ca. 1500 K)

Ti-crystals

I₂

Ti-powder (ca. 800 K)
3.3 Crystal refinement by floating zone melting

- a small slice of the sample is molten and moved continuously along the sample
- impurities normally dissolve preferably in the melt (!! icebergs in salt water don't contain any salt !!)

- segregation coefficient $k$:
  \[ k = \frac{c_{\text{solid}}}{c_{\text{liquid}}} \]
  ($c$: concentration of an impurity)

only impurities with $k < 1$ can be removed by zone melting !!
3.4 Growth of single crystals: Bridgman-Stockbarger-process (moving temperature gradient, vertical or horizontal)
### 3.4 Growth of single crystals: Bridgman-Stockbarger-process

→ preferably: crystal growth of **congruently melting compounds**

<table>
<thead>
<tr>
<th>crystal</th>
<th>mp (°C)</th>
<th>velocity of grad.</th>
<th>container material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>2037</td>
<td>2-8 mm h$^{-1}$</td>
<td>Mo</td>
</tr>
<tr>
<td>FeAl$_2$O$_4$</td>
<td>1790</td>
<td>5-10</td>
<td>Ir</td>
</tr>
<tr>
<td>Cu</td>
<td>1083</td>
<td>6-60</td>
<td>graphite</td>
</tr>
<tr>
<td>AgBr</td>
<td>434</td>
<td>1-5</td>
<td>Pyrex</td>
</tr>
<tr>
<td>Ar (!)</td>
<td>-189</td>
<td>0.5-1.5</td>
<td>Mylar</td>
</tr>
</tbody>
</table>
3.4 Growth of single crystals: Czochralski process: Si (I)

- a rotating seed crystal is raised slowly from a melt with equal composition
The single crystal is ground to a precision diameter and then sliced into wafers 1 mm thick. The wafers are then chemically etched and polished with successively finer polishing abrasives until a defect free mirror finish is achieved.
3.4 Growth of single crystals: Verneuil process

- preferably for high melting oxides (T > 2000 K)
- powdered sample is blown into a oxyhydrogen gas burner

Synthetic corundum crystals obtained by the Verneuil process
3.4 Growth of single crystals: Hydrothermal synthesis

Chemical transport in supercritical aqueous solution (H\textsubscript{2}O: T\textsubscript{k} = 374 °C, p\textsubscript{k} = 217.7 atm)

Autoclave for the growth of SiO\textsubscript{2} single crystals (1 m NaOH, 1500 bar,
T- gradient 400 → 380 °C
1: nutrient (powder), 2: seed crystal,
3: mechanical fixing of crystal
4: product crystal

Lit.: Die Rolle der Hydrothermalsynthese in der präparativen Chemie, A. Rabenau,
Angew. Chem. 97 (1985) 1017
3.5 Chemical Vapor Deposition (CVD)

General term for a variety of methods (including epitaxy and sputtering) to deposit a range of inorganic materials for use in semiconducting devices, ceramic coatings, electrooptic devices etc.

CVD setup for the production of high purity silicon

CVD assembly for the epitaxial growth of $GaAs_{1-x}P_x$
3.5 Physical and chemical methods to produce thin layers of chemical compounds or to clean surfaces

1. "Sputtering": (to sputter: zischen, brutzeln, spritzen ...) - originally: method to clean surfaces, Ar\(^+\)-ions are accelerated in an electrical field and "hit" the target that has to be cleaned; as a consequence surface atoms or molecules are removed from the surface

2. Epitaxy: "Thin" oriented layers (thickness of some µm or nm) are deposited on a "substrate with the same or a similar crystal structure. The deposition starts from gaseous precursors, which condensate or decompose on the surface of the substrate.
3.6 High pressure syntheses

Starting mixture is encapsulated and heated under pressure!

By rapid pressure release and quenching metastable products are eventually stabilized

In general the high pressure phase has a higher density and the coordination numbers (and interatomic distances!) of corresponding atoms are higher than in the low pressure phase, e.g.

SiO$_2$ (Si: CN=4) $\rightarrow$ SiO$_2$ (Si: CN=6) (quartz) (Stishovit, rutile structure)

$\rightarrow$ „pressure-distance-paradoxon“

Diamond anvil cell

about 1000 kbar (100 GPa) (1 bar = $10^5$ Pascal)
3.6 High pressure syntheses: limitations of the reactive volume

Starting mixture is encapsulated and heated under pressure!

By rapid pressure release and quenching metastable products are eventually stabilized.