Gas phase transport reactions

CT	Chemical Transport
CVT	Chemical Vapour Transport
CTR	Chemical Transport Reaction
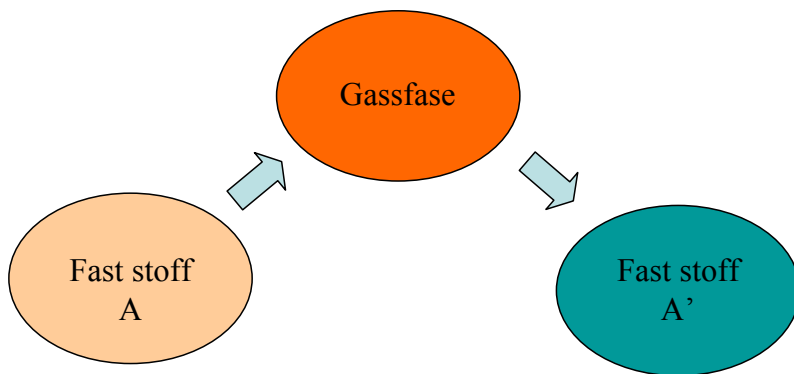
Used to:
Purify materials
Grow single crystals
Increase reaction rates

In chemical transport reactions, solids are transported via a gas phase using a chemical reaction.

The structure of the material is broken down and rebuilt.

Reversible chemical equilibria are utilized.

1

Transport reaction

A(s) + B(g) = AB(g)   ΔH

The reaction must be reversible and have K_{eq} ~ 1 at the operating temperature

Convention: $T_2 > T_1$ (In book: transport from T_1 to T_2)

$\Delta H > 0$ Endothermic   Transport from hot to cold

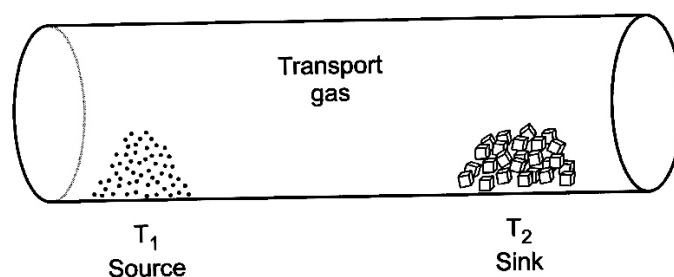$\Delta H < 0$ Exothermic   Transport from cold to hot

Figure 3-1. The principle of chemical transport reactions. The reaction vessel can be open or closed (see text).
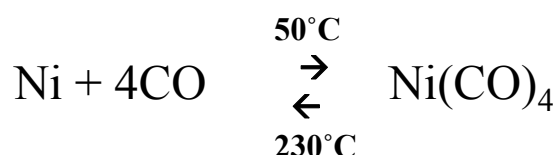
2

Some reactions

Transport in open systems with continuous flow:
Transport in volcanic systems:

$$3Fe_2O_3(s) + 6HCl(g) \leftrightarrow 2FeCl_3(g) + 3H_2O(g)$$

Deposition of Fe_2O_3 at cooler sites.

Mond process: deposition of pure Ni (99.9 – 99.99%

$$Ni + 4CO \quad \underset{230°C}{\overset{50°C}{\underset{\leftarrow}{\rightarrow}}} \quad Ni(CO)_4$$
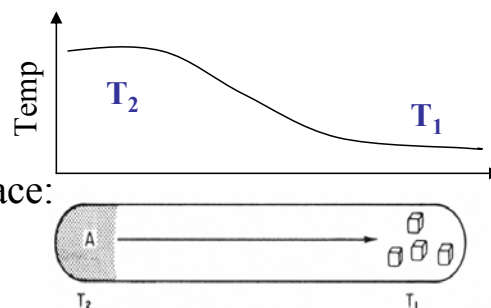
Exothermic reaction. Ni transported from mixture and deposited at 230°C.

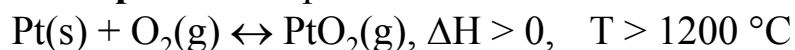> **Polymorphs:** **May stabilize metastable phases by seeding**
>
> **Non-stoichiometric phases** **(oxides, sulfides…): Difficult to reproduce and control. Very dependent on experimental conditions.**
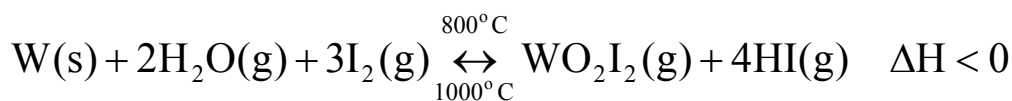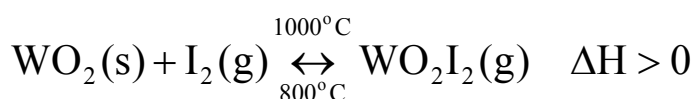

More reactions

Transport: Transport of Pt to a cold zone in a furnace:
$Pt(s) + O_2(g) \leftrightarrow PtO_2(g)$, $\Delta H > 0$, $T > 1200$ °C

Purification: van Arkel Process: (Ti, Hf, V, Nb, Ta, Cr, Fe, Cu, Th,...)
$Cr(s) + I_2(g) \leftrightarrow CrI_2(g)$, $\Delta H < 0$ (Deposition of Cr at a higher temperature)

Separation; W og WO_2: (Deposition of $WO_2(s)$ at 800°C; W(s) at 1000°C)

$$WO_2(s) + I_2(g) \underset{800°C}{\overset{1000°C}{\leftrightarrow}} WO_2I_2(g) \quad \Delta H > 0$$

$$W(s) + 2H_2O(g) + 3I_2(g) \underset{1000°C}{\overset{800°C}{\leftrightarrow}} WO_2I_2(g) + 4HI(g) \quad \Delta H < 0$$

Enhancing kinetics of solid state reactions:
The reaction; $2CaO(s) + SnO_2 \rightarrow Ca_2SnO_4(s)$ is slow
$SnO_2(s) + CO(g) \leftrightarrow SnO(g) + CO_2(g)$
$2CaO(s) + SnO(g) + CO_2(g) \leftrightarrow Ca_2SnO_4(s) + CO(g)$
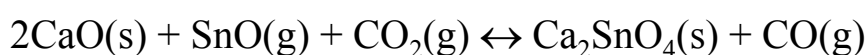
The halogen lamp

The halogen lamp is one of the most important uses of transport reactions.
Incandescence: Black body radiation.
Edison: First incandescent lamp in 1879, carbon filament
Major improvements: Tungsten filament, using gas filled bulb instead of evacuation
Still most of the light is lost as heat (IR). (1.4% in the visible range at 2400˚C)
Advantages of W-filament: Low vapour pressure, melting point 3400˚C, good
mechanical strength at high temperature. However, an increase in temperature from
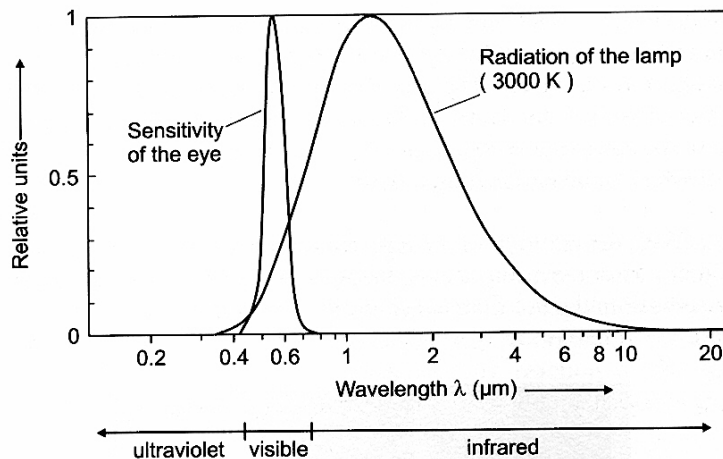e.g. 2527 to 2927˚C decreases the life time by a factor of 100

Figure 3-2. The spectrum of incandescent lamps.
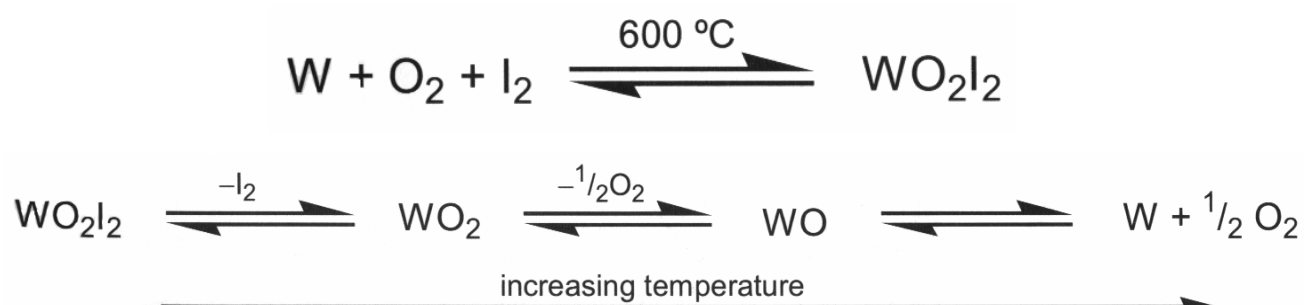

Halogen lamp II

W-filament: Evaporated W is deposited at cold surfaces (inside of bulb).
Blackening the bulb, and thinning the filament (thinner filament increases the
temperature → increases the vapour pressure…

Inert gas filling: Reduces the evaporation of W by inhibiting the transport
process (evaporation, condensation). The large size of the bulbs limits the
pressure used.

Halogens: Adding small amounts of a halogen (usually I_2) results in transport of
tungsten back to the (hot) filament.
Could be this process: $W + I_2 \leftrightarrow WI_2$. But it is more complex:

$$W + O_2 + I_2 \underset{\longleftarrow}{\overset{600\,^{\circ}C}{\longrightarrow}} WO_2I_2$$

$$WO_2I_2 \underset{\longleftarrow}{\overset{-I_2}{\longrightarrow}} WO_2 \underset{\longleftarrow}{\overset{-\frac{1}{2}O_2}{\longrightarrow}} WO \underset{\longleftarrow}{\longrightarrow} W + \tfrac{1}{2}\,O_2$$

increasing temperature →

Halogen lamp III

The reactions require a minimum temperature of 600C at the bulb surface. Thus the halogen lamp is small. This also means that it may be thicker, and operates at higher internal pressures.
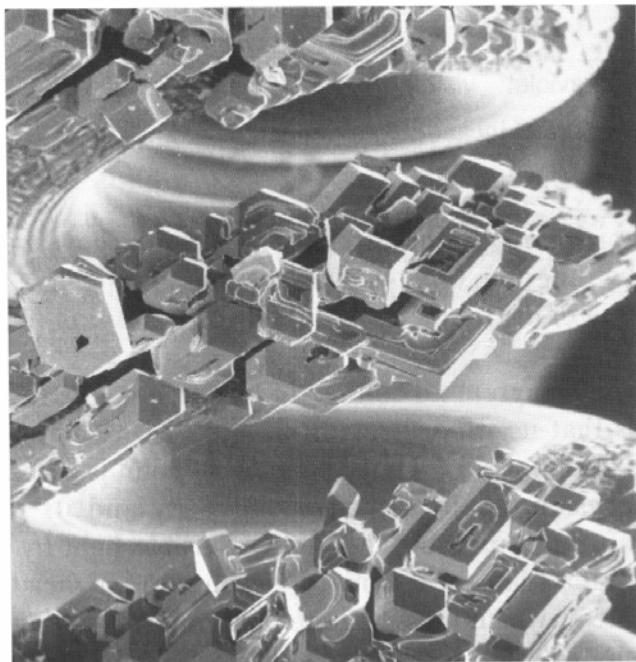

This is, however, not a self-healing process.
W is still transported from hot spots at the filament to cooler spots (at 3000˚C)
But it allows operation at higher temperatures for a long time.

Figure 3-3. Deposition of tungsten crystals on the tungsten filament of a halogen lamp (130-fold magnification).

Metal halide (arc) lamp

Tube quartz glass or alumina, Tungsten electrodes. Alkali/lanthanide halide system DyI_3, TmI_3, HoI_3: Large number of emission lines.

Gaseous species: e.g. $NaDyI_4$, Na_2DyI_5
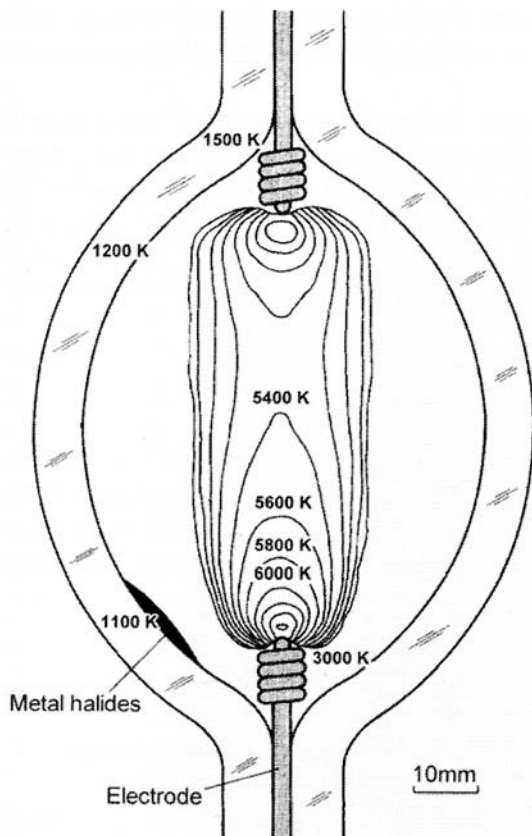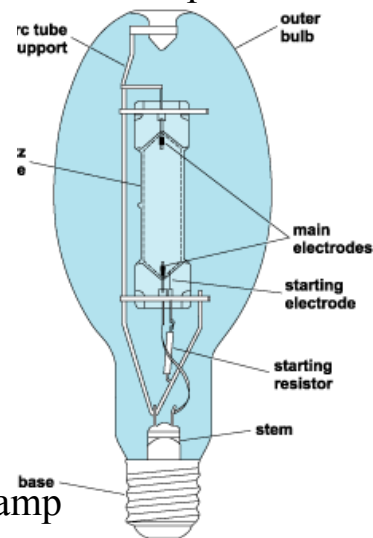Dissociation in the arc (to elements or ionized species), recombination in cooler parts.

Figure 3-4. Arc tube of a metal halide lamp with temperature distribution under operating conditions.

Mercury vapour lamp

Transport reactions

Four steps in ideal transport reaction:
1. Chemical reaction at the source (equilibrium between gaseous and condensed phase)
2. Mass transport by diffusion of gaseous species from the source to the sink.
3. Deposition of solid at the sink
4. Diffusion of gaseous transport agent back to the source

Diffusion limited reaction. Convection and Stefan flow (due to different amounts of molecules) may be important

$$A(s) + B(g) = AB(g) \qquad \Delta H$$

AB(g)   Diffusjon   B(g)
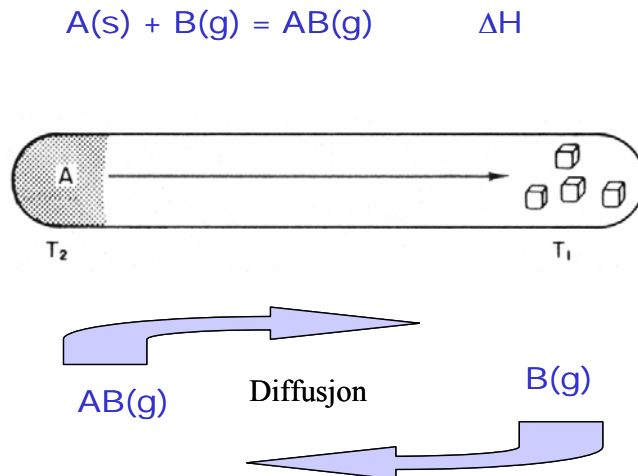
Choice of transporting agent

May in principle be chosen from thermodynamic data. All species and reactions must be known! Reactions are usually far more complex than indicated from the overall chemical equation.

Halogens are often used to transport metals.

Metal oxides are often transported using hydrogen halides (In some cases halogens may be used)

Table 3-1. Transport reactions of chromium compounds

Transported compound	Transport agent	Gas-phase species
Cr	I_2	CrI_2
CrX_3 (X = Cl, Br, I)	X_2	CrX_4
$CrCl_3$	$AlCl_3$	$CrAl_3Cl_{12}$
Cr_2O_3	O_2/Cl_2	CrO_2Cl_2
Cr_2O_3	H_2O/Cl_2	$CrO_2Cl_2 + HCl$
Cr_2O_3	$H_2O/HgCl_2$	$CrO_2Cl_2 + Hg + HCl$
$CoCr_2O_4$ (spinel)	Cl_2	$CrO_2Cl_2 + CoCl_2$
$Cr_2(SO_4)_3$	HCl	$CrO_2Cl_2 + SO_2 + H_2O$
$Cr_2P_2O_7$	I_2/P_4	$CrI_2 + P_4O_6$
$CrSi_2$	I_2	$CrI_2 + SiI_4$

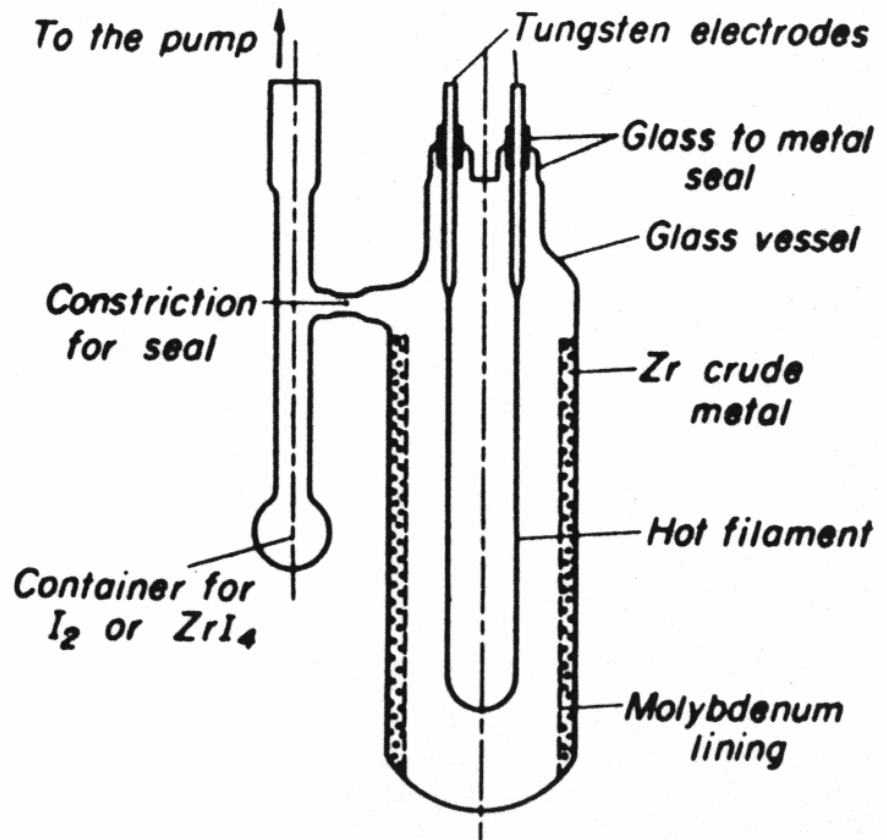# The van Arkel or van Arkel-de Boer process

Preparation of pure metals, Ti, Hf, V, Nb, Ta, Cr, Fe, Cu, Th,...

$Cr(s) + I_2(g) \leftrightarrow CrI_2(g)$, $\Delta H < 0$
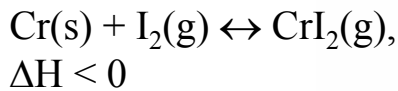
(Deposition at a hot filament)

Calculation of reaction rates

Calculation of growth rates may be complicated by e.g.:
•All reactions and species must be known
•Local equilibria must be established (s) $\leftrightarrow$ (g)
Transport may not be entirely diffusion, but may be influenced by:
Gas phase equilibria, e.g. $2S_2 \leftrightarrow S_4(g)$ (temperature dependent)
Convection in the ampoule
Changes in the number of gas molecules (Stefan flow)
Kinetics of dissolution and condensation
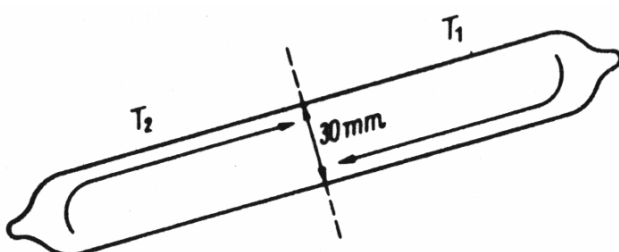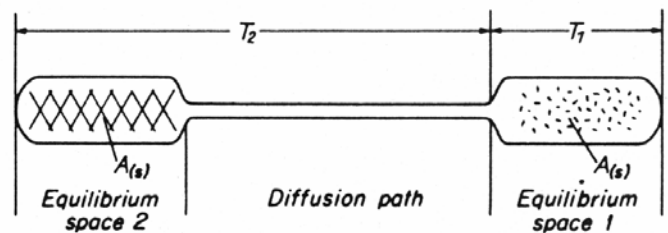
Reducing convection

FIG. 9. The transport of solid substances with gas motion by diffusion. Simplified theoretical diagram.

FIG. 5. Gas motion by thermal convection.

Growth rates

i A(s,l) + k B(g) ↔ j C(g)

$$n_a = \frac{i}{j} \cdot \frac{\Delta P_C}{\Sigma P} \cdot \frac{D_0 \cdot \Sigma P_0 \cdot T^{0.8} \cdot q \cdot t}{T_0^{1.8} \cdot s \cdot R}$$

n_a Number of moles transported of compound A

i,j   Coefficients for the reactions

ΔP_C Change in the partial pressure of species C

ΣP Total pressure in thye ampoule

q   Cross section (area) of the diffusion path

t   Duration of transport reaction

s   Diffusion length

R   The gas constant

$$n_a = \frac{i}{j} \cdot \frac{\Delta P_C}{\Sigma P} \cdot \frac{T^{0.8} \cdot q \cdot t}{s} \cdot 1.8 \cdot 10^{-4} \quad \text{(mol)}$$

13

Yield $Q = \dfrac{n_A(\text{målt})}{n_A(\text{beregnet})}$

(I)   The heterogenic reactions are rate limiting

(II)   Diffusion is the rate limiting step

(III) Convection contributes to the kinetics
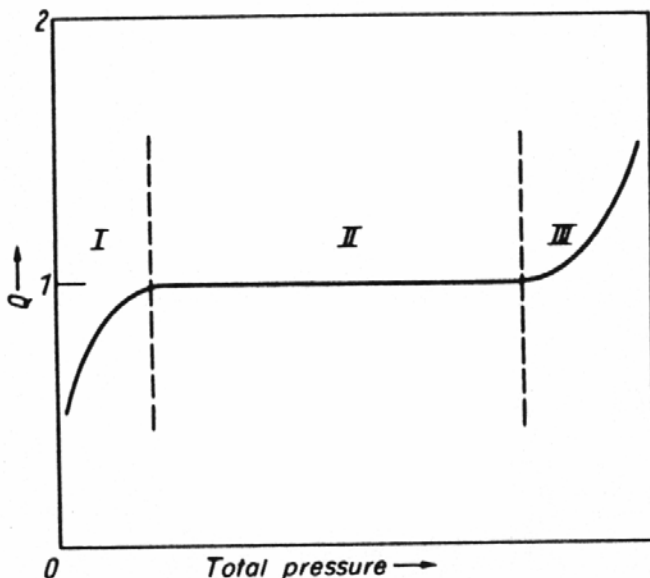
The diffusion constant depends on temperature and gas mixture. If there are no H or He in the gas mixture, the error by setting $D_0 = 0.1$ cm^2/s is (relatively) small

TABLE I

DIFFUSION COEFFICIENTS D_0 FOR $\Sigma P_0 = 1$ ATM AND $T_0 = 273°$K

Gas pair		D_0 (cm² sec⁻¹)
H₂	+ O₂	0.70
	H₂O	0.69
	CO	0.65
	CH₄	0.63
	Br₂	0.56
	CO₂	0.54
	CS₂	0.37
	CCl₄	0.30
N₂ (also air or O₂)	+ H₂O	0.22
	NH₃	0.20
	Hg	0.11
	CS₂	0.09
	I₂	0.07
	CCl₄	0.06
CO₂	+ H₂O	0.13
	CO	0.13
	Br₂	0.09
	CS₂	0.06
	(C₂H₅)₂O	0.05

Reaction conditions

Typical:

Temperature: 300 – 1200 °C

Temperature gradient: 10 – 100 °C

Total pressure: 0.5 – 10 atm

Transport agent: 1 – 5 mg per ml ampoule volume

Time: 2 hours – 1 month

The Ampoule: - Material: Quartz (Nb, Mo)

   - Length: 10 – 20 cm

   - Diameter: 0.8 – 2.5 cm

Crystal quality:

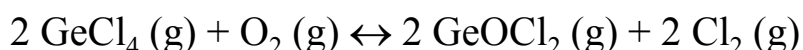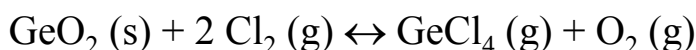Crystal size (depends on the number of nuclei): Small ΔT

Defects: Low temperature, low transport rate

Chemical purity (Incorporation of transporting agent in crystals:
Large chemical differences (e.g. CdS, I$^-$ on S^{2-} position)

Transport of GeO$_2$

$$GeO_2\,(s) + 2\,Cl_2\,(g) \leftrightarrow GeCl_4\,(g) + O_2\,(g)$$

$$2\,GeCl_4\,(g) + O_2\,(g) \leftrightarrow 2\,GeOCl_2\,(g) + 2\,Cl_2\,(g)$$

| Temperatur Specie	800 °C aktivitet	820 °C aktivitet	880 °C aktivitet	900 °C aktivitet
Cl$_2$	4.35×10^{-1}	4.15×10^{-1}	3.59×10^{-1}	3.41×10^{-1}
O$_2$	2.81×10^{-1}	2.90×10^{-1}	3.14×10^{-1}	3.21×10^{-1}
GeCl$_4$	2.77×10^{-1}	2.85×10^{-1}	3.02×10^{-1}	3.05×10^{-1}
GeOCl$_2$	6.46×10^{-3}	9.09×10^{-3}	2.33×10^{-2}	3.11×10^{-2}
Cl	3.67×10^{-4}	4.63×10^{-4}	8.79×10^{-4}	1.07×10^{-3}
GeCl$_3$	4.27×10^{-5}	6.44×10^{-5}	2.00×10^{-4}	2.83×10^{-4}
ClO	1.93×10^{-5}	2.36×10^{-5}	4.09×10^{-5}	4.83×10^{-5}
Ge$_2$OCl$_6$	5.12×10^{-6}	4.41×10^{-6}	2.79×10^{-6}	2.38×10^{-6}
GeCl$_2$	6.30×10^{-9}	1.31×10^{-8}	1.01×10^{-7}	1.89×10^{-7}
ClO$_2$	6.76×10^{-8}	8.22×10^{-8}	1.39×10^{-7}	1.63×10^{-7}
Cl$_2$O	2.46×10^{-8}	2.86×10^{-8}	4.29×10^{-8}	4.83×10^{-8}
O	3.36×10^{-10}	5.74×10^{-10}	2.54×10^{-9}	4.03×10^{-9}
GeO	1.13×10^{-12}	3.24×10^{-12}	6.07×10^{-11}	1.51×10^{-10}
GeCl	1.23×10^{-17}	4.33×10^{-17}	1.45×10^{-15}	4.32×10^{-15}
Cl$_3$	1.05×10^{-18}	2.34×10^{-18}	2.15×10^{-17}	4.26×10^{-17}
Cl$_4$	2.20×10^{-19}	4.23×10^{-19}	2.56×10^{-18}	4.44×10^{-18}
Ge$_2$O$_2$	2.50×10^{-22}	1.42×10^{-21}	1.82×10^{-19}	8.21×10^{-19}
Ge$_3$O$_3$	1.07×10^{-31}	1.21×10^{-30}	1.06×10^{-27}	8.67×10^{-27}

Tabell Error! No text of specified style in document.**.1. Aktiviteten til speciene beregnet ved 3.75 atm totattrykk ved forskjellige temperaturer. Startbetingelser er 1 mol GeO$_2$, 0.1 mol Cl$_2$, resten av speciene har initialverdi lik 0.**

Temperature gradients in a two zone furnace
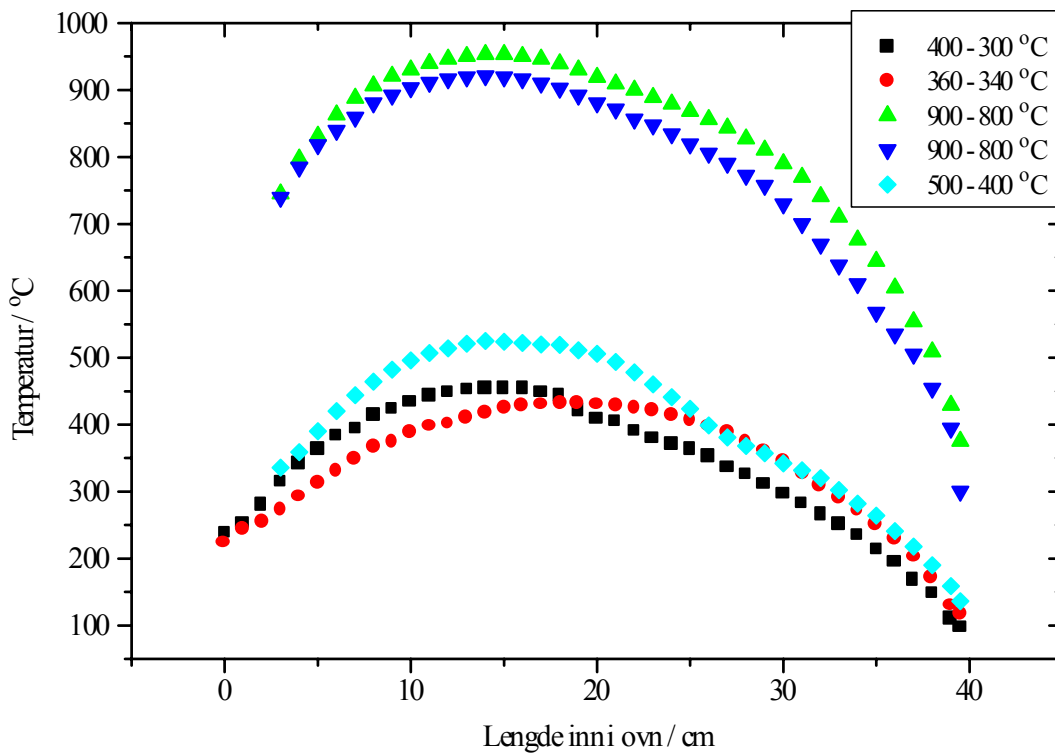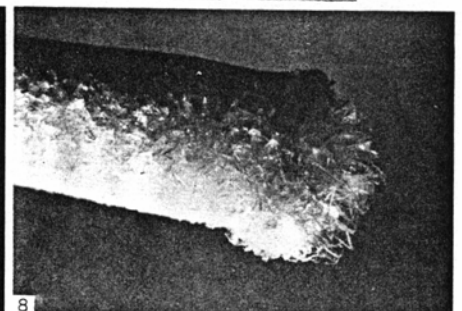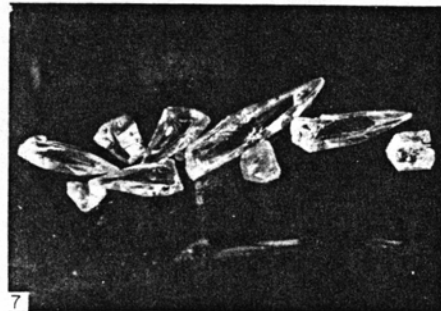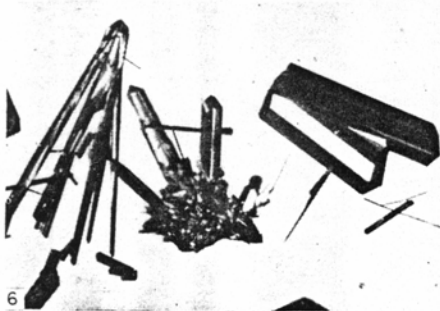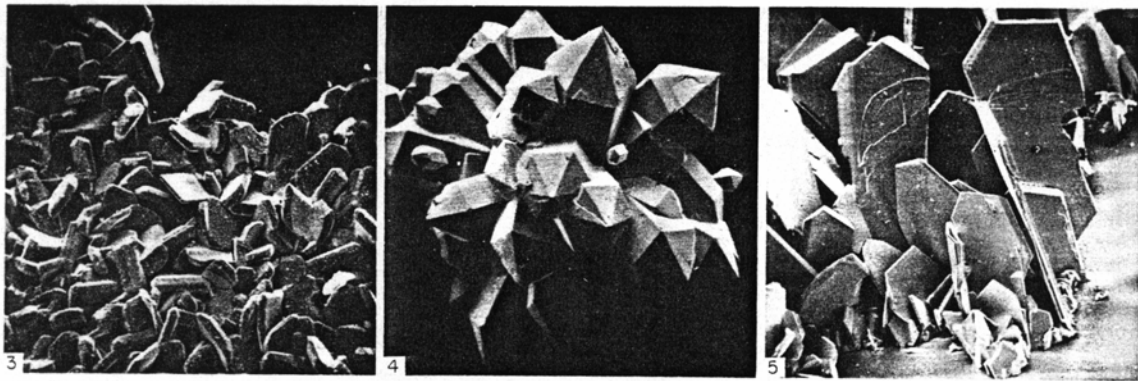
3. CsNb₄Br₁₁, transported with NbBr₅. Crystal size about 0.2 mm (Broll *et al.*, 1969.)

4. ReO₂, transported with I₂. Diameter of the crystal block about 1 mm (Schäfer and Bode, 1967.)

5. TaS₂, transported with S. Crystal size ≧ 10 mm. (Schäfer *et al.*, 1968.)

6. RuO₂, transported with O₂. The thickest crystal is 6 mm long (Schäfer *et al.*, 1963).

7. Al₂S₃, transported with I₂. Crystal size up to about 10 mm. (Schäfer, 1962, Schäfer and Jagusch, 1966.)

8. SiO₂ (tridymite), transported with HF. Clear crystals up to 3 mm. (Gruehn, 1967.)

9. CdO, transported with I_2. Crystals up to about 0.8 mm. (Schäfer and Fuhr, 1964.)

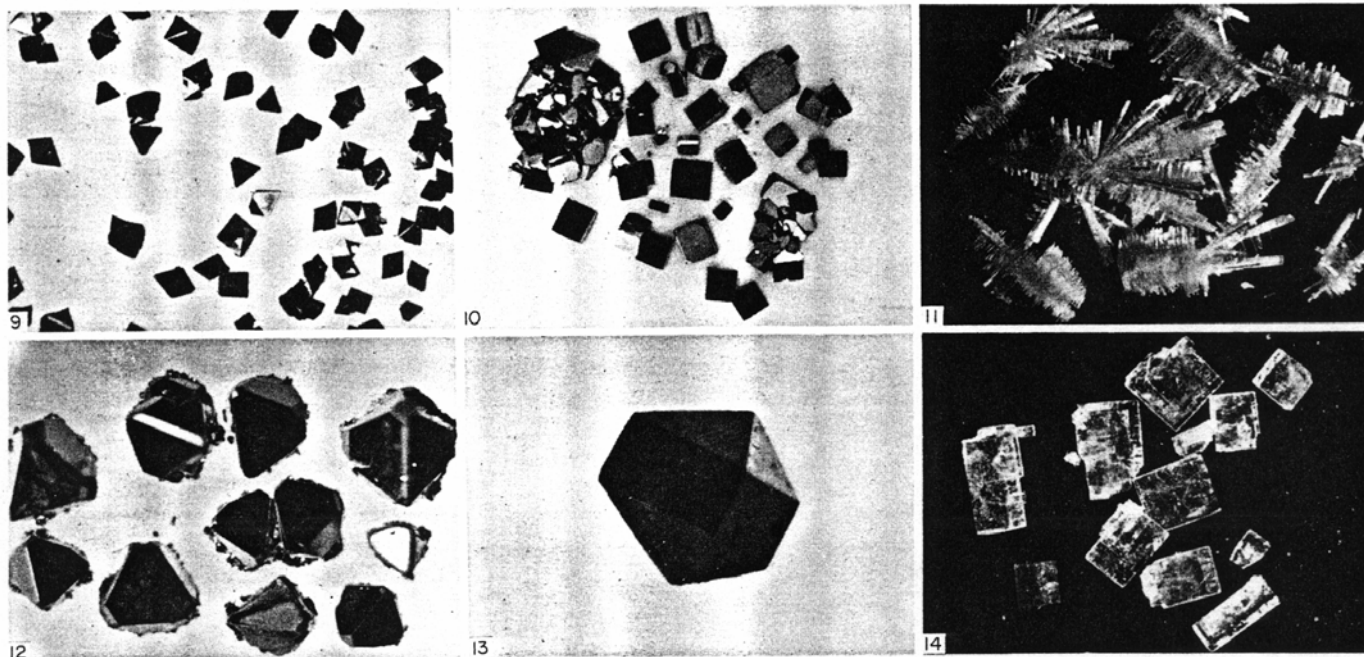10. ReO₃, transported with I_2. Crystal size up to 1 mm. (Schäfer and Bode, 1967.)

11. Ti₂Nb₁₀O₂₉ (monoclinic), transported with NbCl₅. Length of the crystal needles is about 5 mm. (Gruehn et al., 1967.)

12. Nb₃Sb, transported with I_2. Crystal size up to 3 mm. (Schäfer and Fuhr, 1965.)

13. NbO₂, transported with I_2. Crystal size 1 mm. (Schäfer and Hüesker, 1962.)

14. Nb₂O₅, in the P modification, transported with NbCl₅. Crystal size 1–2 mm. (Schäfer et al., 1966.)

TABLE I

CHEMICALLY TRANSPORTED TERNARY AND QUATERNARY COMPOUNDS

Compound	Transporting agent	Reference
RbNb₄Cl₁₁, CsNb₄Cl₁₁	NbCl₅	Broll et al. (1969)
VCl₂Br	Br₂	McCarley et al. (1964)
VBr₂I	I₂	McCarley et al. (1964)
TaOCl₂	TaCl₅	Schäfer et al. (1961)
MoOCl₂	MoCl₅	Schäfer and Tillack (1964)
WOBr₂	WOBr₄	Tillack and Kaiser (1969)
NbOI₂	I₂	Schäfer and Gerken (1962)
Me₃B₇O₁₃X (X = Cl, Br, I; Me = Fe, Co, Ni)	HX + H₂O	Schmid (1965)
NbS₂Cl₂ (NbY₂X₂, Y = S, Se; X = Cl, Br, I)	NbCl₄	Schäfer and Beckmann (1966)
SbSBr	Br₂	Klazer and Horák (1968)
BiSBr	Br₂	Kozáková et al. (1966)
SbSI	I₂	Kern (1962), Grigas (1968a)
SbSeBr	Br₂	Klazer and Horák (1968)
SbSeI	I₂	Nejezchleb and Horák (1968), Grigas (1968b)
BiTeBr	Br₂	Horák and Rodot (1968)
CuCr₂Y₄X (X = Cl, Br; Y = S, Se)	Halogen	Miyatani et al. (1968)
MeGeO₃ (Me = Mn, Fe, Co)	HCl (NH₄Cl)	Royen and Forwerg (1962, 1963)
MeTiO₃ (Me = Mg, Ni)	Cl₂	Emmenegger (1968)
MeNbO₄ [Me = Fe(III), Cr(III)]	Cl₂ + NbCl₅	Emmenegger (1968); Emmenegger and Petermann (1968)
FeTaO₄	Cl₂ + TaCl₅	Emmenegger (1968)
CrTaO₄	Cl₂	Emmenegger (1968)
MeMoO₄ (Me = Mg, Mn, Co, Ni)	Cl₂	Emmenegger (1968)
MeWO₄ (Me = Mg, Mn, Fe, Co, Ni, Zn)	Cl₂	Emmenegger (1968)
Co₂SnO₄	Cl₂	Emmenegger (1968)
MeCr₂O₄ (Me = Mn, Co, Ni)	Cl₂	Emmenegger (1968)
MeFe₂O₄ (Me = Mn, Co, Ni)	HCl	Curtis and Wilkinson (1965)
MeFe₂O₄ (Me = Mg, Mn, Co, Ni)	HCl	Kleinert (1963, 1964)
MeNb₂O₆ (Me = Ca, Co, Ni)	Cl₂	Emmenegger and Petermann (1968)
MeNb₂O₆ (Me = Mg, Zn)	HCl	Emmenegger and Petermann (1968)
MeNb₂O₆ (Me = Fe, Mn)	Cl₂ + NbCl₅	Emmenegger and Petermann (1968)
MeTa₂O₆ (Me = Mg, Mn, Co)	Cl₂	Emmenegger (1968)
NiTa₂O₆	Cl₂ + TaCl₅	Emmenegger (1968)
ZrOS	I₂	Nitsche (1967)

TABLE I (continued)

Compound	Transporting agent	Reference
ZrSiS	I₂	Nitsche (1967)
MeGeS₄ (Me = Fe, Mn)	I₂	Nitsche (1967)
MeIn₂S₄ (Me = Zn, Cd, Hg)	I₂	Nitsche (1960); Nitsche et al. (1961)
MeIn₂S₄ (Me = Mn, Co)	I₂	Nitsche (1967)
MeGa₂S₄ (Me = Zn, Cd, Hg)	I₂	Nitsche et al. (1961)
MeCr₂S₄ (Me = Mn, Zn, Cd)	AlCl₃ (HCl)	Lutz and von Lovász (1968)
CdCr₂S₄	Cl₂	Berger and Pinch (1967)
CoCr₂S₄	HCl (NH₄Cl)	Nitsche (1967)
Cu₂MeY₄ (Me = Nb, Ta; Y = S, Se)	I₂	Nitsche and Wild (1967)
Cu₃NbS₄, Cu₃TaS₄	I₂	Nitsche (1967)
Cd₄SiS₆	I₂	Kaldis et al. (1967)
ZrSiSe	I₂	Nitsche (1967)
MeIn₂Se₄ (Me = Zn, Cd)	I₂	Nitsche (1960); Nitsche et al. (1961)
MeGa₂Se₄ (Me = Zn, Cd)	I₂	Nitsche et al. (1961)
CdCr₂Se₄	Br₂	Scholz (1966)
Cd₄SiSe₆	I₂	Kaldis et al. (1967)
MeCu₂SiS₄ (Me = Zn, Cd, Fe)	I₂	Nitsche et al. (1967)
MeCu₂GeS₄ (Me = Zn, Cd, Fe, Mn, Ni)	I₂	Nitsche et al. (1967)
MeCu₂SnS₄ (Me = Zn, Cd, Fe)	I₂	Nitsche et al. (1967)
ZnCu₂GeSe₄	I₂	Nitsche et al. (1967)
ZnSiP₂	I₂	Valov and Usakova (1968)
CdSiP₂	Cl₂, SiCl₄	Valov and Plecko (1967), (1968)

TABLE II

Examples of Solid Solution Formation by Chemical Transport[a]

Solid solution system	Transporting agent	Reference
Nb_3Cl_8–Nb_2Cl_8	$NbCl_5$	Schäfer and Dohmann (1959b)
ZnS–CdS	I_2	Davis and Lind (1968)
ZnS–MnS	I_2	Nitsche et al. (1961)
TiS_2–VS_2	I_2	Nitsche (1967)
TiS_2–NbS_2	I_2	Nitsche (1967)
TiS_2–TaS_2	I_2	Nitsche (1967)
GaAs–InAs	Cl_2	Sirrine (1964); Minden (1965)
2GaAs–$ZnSiAs_2$	Cl_2, I_2	Averhieva et al. (1967)
2GaAs–$ZnGeAs_2$	Cl_2, I_2	Averhieva et al. (1967)
SnO_2–SnS_2	I_2	Nitsche (1967)
TiS_2–$TiSe_2$	I_2	Nitsche (1967)
ZrS_2–$ZrSe_2$	I_2	Nitsche (1967)
$CdCr_2S_4$–$CdCr_2Se_4$	I_2 + $AlCl_3$	Pickardt (1970)
TiS_2–$TiTe_2$	I_2	Nitsche (1967)
GeSe–GeTe	I_2	Muir and Cashman (1968)
ZnSe–GaAs	I_2	Ku and Bodi (1968)
Cu_2GeSe_3–3GaAs	I_2, Cl_2	Averhieva et al. (1967)
GaP–GaAs	I_2	Pizzarello (1962); Ku (1963); Hull (1964)
	Cl_2	Holonyak et al. (1961)
	H_2O	Gottlieb (1965); Purohit (1968)
InP–InAs	I_2	Egorov et al. (1967)

[a] Frequently, the given solid solutions were synthesized so that the mechanical mixture of the binary compounds served as the reactant for transport. Sometimes, however, the previously prepared solid solution was used as reactant, too.

TABLE III

Reactions Where the Reaction Product Is Transportable[a]

Reaction	Transporting agent	Reference
$Zn_l + 0.5S_{2,g} = ZnS$	I_2	Schäfer (1962)
$Zn_l + 0.5Se_{2,g} = ZnSe$	I_2	Schäfer (1962)
$Cd_l + 0.5S_{2,g} = CdS$	I_2	Schäfer (1962)
$Cd_l + 0.5Se_{2,g} = CdSe$	I_2	Schäfer (1962)
$2Al_l + 1.5S_{2,g} = Al_2S_3$	I_2	Compare with Schäfer (1962) and Schäfer and Jagusch (1966)
$2Al_l + 1.5Se_{2,g} = Al_2Se_3$	I_2	Compare with Schäfer (1962) and Schäfer and Jagusch (1966)
$Ru_s + O_2 = RuO_2$	O_2	Schäfer et al. (1963)
$Ir_s + O_2 = IrO_2$	O_2	Schäfer and Heitland (1960)

[a] In these cases the formation of a surface layer is prevented.

TABLE IV

Separation by Means of Different Transport Directions

Product deposited at T_1	at T_2	Temperature gradient T_1/T_2 (°C)	Transporting agent	Reference
CrTe	Cr	850/1025	I_2	Schäfer (1962)
Cu	Cu_2O	600/900	HCl	Schäfer and Etzel (1957)
CuO	Cu_2O	700/800	HCl	Schäfer and Jagusch (1966); Schäfer (1968)
$NbAs_2$	NbAs	850/1050	I_2	Schäfer and Fuhr (1965)
WO_2	W	800/1000	I_2 + H_2O	Dettingmeijer et al., (1969)