# Chemical Vapor Transport Reactions–Methods, Materials, Modeling

Peer Schmidt, Michael Binnewies,
Robert Glaum and Marcus Schmidt

Additional information is available at the end of the chapter

## 1. Introduction

### 1.1. Chemical vapor transport reactions

A variety of processes of crystal growth proceeds via the gas phase. A short comparative overview on gas phase transports is given here. However, in the main we deal with the concept of Chemical Vapor Transport Reactions [1, 2]. The term "*Chemical Vapor Transport*" (CVT) summarizes heterogeneous reactions which show one shared feature: a condensed phase, typically a solid, has an insufficient pressure for its own volatilization. But the pertinent phase can be volatilized in the presence of a gaseous reactant, the *transport agent*, and deposits elsewhere, usually in the form of crystals. The deposition will take place if there are different external conditions for the chemical equilibrium at the position of crystallization than at the position of volatilization. Usually, different temperatures are applied for volatilization and crystallization, Figure 1.
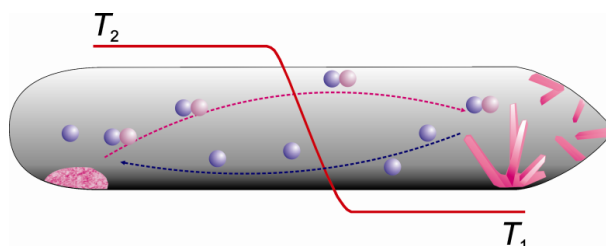


**Figure 1.** Scheme of CVT experiments for crystallization of solids in a temperature gradient.

Chemical vapor transport reactions address the formation process of pure and crystalline solids. Especially, the growth of single-crystalline material is of particular value because, among other things, it allows the determination of the crystal structure by diffraction methods. Beyond the aspect of basic research, chemical vapor transport reactions have also gained practical significance: they form the basis of the operating mode of halogen lamps. Furthermore, an industrial process is based on a chemical transport reaction, the Mond-Langer-Process for the production of ultrapure nickel [3]. Chemical vapor transports likewise occur in nature forming minerals without human influence, in particular at places of high temperatures. Bunsen was the first who observed and described it [4]. He noticed that the formation of crystalline $Fe_2O_3$ is associated with the presence of volcanic gases which contain gaseous hydrogen chloride. Van Arkel and de Boer were the first scientists who carried out specific transport reactions in the laboratory from 1925 onwards [5]. They were motivated by the huge interest in finding a process to fabricate pure metals like titanium at that time [6]. Van Arkel and de Boer used the so called *glowing wire method*. In the process, the contaminated metal *M* (e.g. a metal of the $4^{th}$ group) transforms into a gaseous metal iodide ($MI_n$) in the presence of iodine as the transport agent. The iodide is formed at the metal surface in an exothermic reaction and vaporizes completely, thus reaching a glowing wire which was heated up to high temperatures. On the glowing wires surface, the back reaction (that is the endothermic reaction) is favored by Le Chatelier's principle. That way the decomposition of the metal iodide via the metals deposition proceeds and the metal is deposited on the hot wire.

A systematic research and description of chemical transport reactions was carried out by Schäfer in the 1950s and 1960s [1]. It became apparent that pure and crystalline species of various solids could be made with the help of chemical transport reactions: metals, metalloid, and intermetallic phases as well as halides, chalcogen halides, chalcogens, pnictides and many others. The current knowledge comprises of thousands of different examples for chemical vapor transport reactions. The results of different periods of investigations are recorded in some review articles [7-13]. Besides, the monographs [1, 2] and an extensive book chapter [14] give an overview on principles and applications of chemical transport reactions referred to the pertinent period of knowledge. To date the chemical vapor transport method developed to be an important and versatile preparative method of solid state chemistry.

Schäfer's endeavour also showed that chemical transport reactions follow thermodynamic regularities [15]; kinetic effects are rarely observed which makes a general description easier. Subsequently, the thermodynamic approaches for detailed description of chemical vapor transports became more sophisticated [16-22]. As a result, complex models for the description of vapor transports of phase mixtures, phases with variable composition, and transports with deposition sequences were established - the "Extended transport model" [18-21] and the "Co-operative transport model" [22]. Thus, the understanding of chemical vapor transport reactions is well developed; predictions on alternative transport agents, optimal reaction conditions and the amount of transported substance are possible and fairly easy accessible via computer programs [23, 24]. Indeed, the proper handling of these programs requires a profound knowledge on thermodynamic data (enthalpy, entropy, heat capacity) of all condenses and gaseous substances that are involved.

The following section shall provide an extensive overview on both principles and mechanisms of chemical vapor transport reactions and on characteristic examples of crystal growth of different substance classes by CVT. A simple thermodynamics basis is given in order to set you in ability to estimate the conditions of vapor transport experiments by own calculations; more complex calculations methods are presented for advanced investigations. Not at least, a short introduction for performing different CVT experiments (ampoule technique, oven setup, determination of transport rates, investigation of transport sequences,…) is given.

## 2. Vapor transport methods and principles

### 2.1. Overview on vapor transport methods

A vast number of reactions involving gas phases hardly differ from each other: If a condensed substance encounters a temperature gradient, it moves from the place of dissolution via the gas phase to the place of deposition, from **source** to **sink**. However, we do not "see" how the substance is led to the gas phase and deposited at another place. The mechanisms of gas phase transports can be deduced from experimental determination of the gas phase composition and/or from thermodynamic considerations of the pertinent heterogeneous equilibria between the solid and the gas phase [25].

**Sublimation**: Sublimations occurs without decomposition of the initial solid by forming only one dominating gas species. Substances showing sublimation are often solids constituting of molecular units, which are "bonded" by only weak interactions. The much stronger (covalent) bond in the molecular unit persist even under external energy stress, and the molecule can sublime undecomposed. Iodine, $I_2$ is a concise example of sublimation.

$$I_2(s) \rightleftharpoons I_2(g) \tag{1}$$
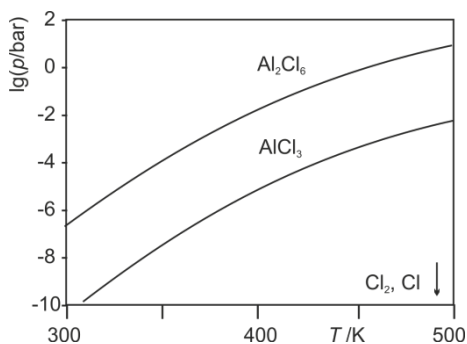


**Figure 2.** Composition of the gas phase of sublimation of $AlCl_3$.

The other possible gas species in the system, I(g) is of less importance due to the significantly lower partial pressures at the temperature of sublimation.

Saline solids can sublime, too. A well-known example is aluminum(III) chloride which is present in the gas phase in large proportion in form of dimeric molecule $Al_2Cl_6$, Figure 2. The additional systems gas species, such as $AlCl_3(g)$, $Cl_2(g)$, and $Cl(g)$ show significantly lower partial pressures at the given temperature and thus not take part in the evaporation process.

$$2\,AlCl_3\,(s) \rightleftharpoons Al_2Cl_6\,(g) \tag{2}$$

In a generalized form, the sublimation of a compound $AB_x$ is described by equilibrium (3).

$$AB_x\,(s) \rightleftharpoons AB_x\,(g) \tag{3}$$

**Decomposition sublimation**: If there is no stable molecular unit which is evaporable, a solid can decompose into various gaseous products while heating. Changing the equilibrium conditions, the initial solid can be recovered out of such a gas phase. This is called decomposition sublimation.

The gas phase transport of bimuth(III) selenide - $Bi_2Se_3$, an important constituent for thermoelectric materials - shows the characteristic of that. It decomposes into stoichiometric amounts of BiSe(g) and $Se_2(g)$ in the vapor phase, the molecule of the initial composition $Bi_2Se_3(g)$ does not occur in evaporation process, Figure 3. During cooling, the gas phase condenses completely and solid solid bimuth(III) selenide is formed (4).

$$Bi_2Se_3\,(s) \rightleftharpoons 2BiSe\,(g) + 1/2\,Se_2\,(g) \tag{4}$$
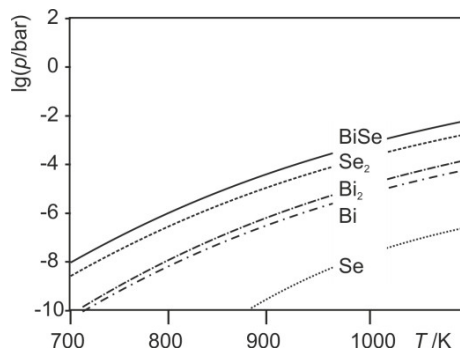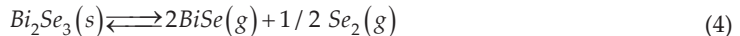


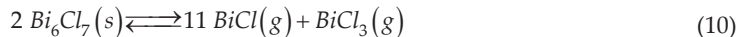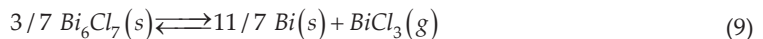**Figure 3.** Composition of the gas phase of decomposition sublimation of $Bi_2Se_3$.

As a generalization, the decomposition sublimation of a compound $AB_x$ can be described by the equilibria (5) or (6), respectively.

$$AB_x \Longleftrightarrow A(g) + xB(g) \qquad (5)$$

$$AB_x \Longleftrightarrow AB_y(g) + (x-y)B(g) \qquad (6)$$

The gas phase transport of $Bi_2Se_3$ by decomposition sublimation gives an example for congruent dissolution and condensation. Thus, a solid of always the same, constant composition is deposited. Nevertheless, a decomposition sublimation can be incongruent, too. Often, the product of an incongruent decomposition sublimation has the same composition as the initial solid. A simple example of this is copper(II) chloride. If heated at a running pump to several hundred degrees, the steam that is built in subsequent equilibria (7) and (8) contains the molecules $CuCl$, $Cu_3Cl_3$, $Cu_4Cl_4$ and $Cl_2$.

$$CuCl_2(s) \Longleftrightarrow CuCl(s) + 1/2\ Cl_2(g) \qquad (7)$$

$$CuCl(s) \Longleftrightarrow CuCl(g) \qquad (8)$$
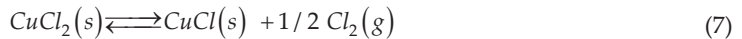
The mechanism of decomposition sublimation is even more complex in the case of $Bi_6Cl_7$ [25, 26]. The initial solid is decomposed into a second solid – here elemental bismuth – and the dominating gas species $BiCl_3$ in equilibrium (9). Thereby, the compositions of the gas phase and thus the "solubility" of all components is unequal the initial composition of the solid, Figure 4.

$$3/7\ Bi_6Cl_7(s) \Longleftrightarrow 11/7\ Bi(s) + BiCl_3(g) \qquad (9)$$

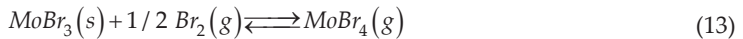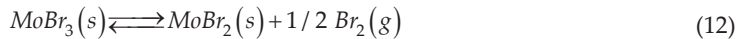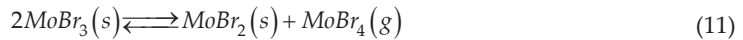$$2\ Bi_6Cl_7(s) \Longleftrightarrow 11\ BiCl(g) + BiCl_3(g) \qquad (10)$$

Nevertheless, the gas phase transport of $Bi_6Cl_7$ is realized by a second, subordinated equilibrium (10). In this case, the composition of the deposited solid strongly depends on the experimental conditions: Congruent deposition of $Bi_6Cl_7$ only occurs with low temperature gradients between source and sink. At higher temperature gradients pure $BiCl_3$ is deposited.

As has been shown, the mechanism of gas phase transport will get more complicated if the decomposition leads to a further condensed solid and a reactive gas phase. Subsequent, auto transport processes can result.
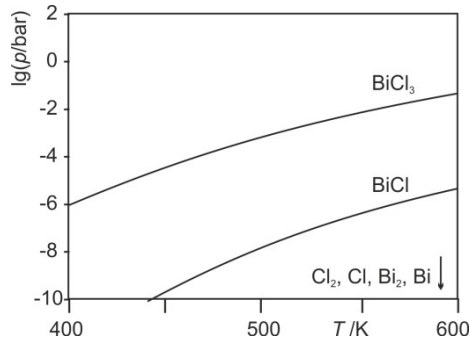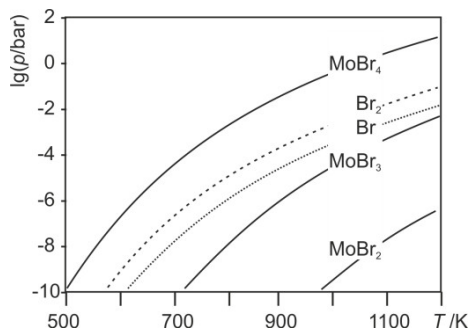
**Figure 4.** Composition of the gas phase of decomposition sublimation of $Bi_6Cl_7$.

**Auto transport**: The auto transport resembles the appearance of sublimation or decomposition sublimation. Nevertheless, the transported solid does not generate an effective partial pressure on its own. Rather, a transport agent is formed by (incongruent) thermal decomposition of the solid and the substance is transferred into the gas phase at a higher temperature without the addition of an external transport agent. The crystallization of $MoBr_3$ serves as an example of auto transport processes. The compound decomposes incongruently under formation of solid $MoBr_2(s)$ releasing a gas phase of the dominant species $MoBr_4$ and $Br_2$ in equilibria (11) and (12), see Figure 5. The heterogeneous equilibria of $MoBr_4$ and $Br_2$ with the initial solid $MoBr_3$ can lead at higher temperature to the vapor transport equilibrium (13).

$$2MoBr_3(s) \rightleftarrows MoBr_2(s) + MoBr_4(g) \tag{11}$$

$$MoBr_3(s) \rightleftarrows MoBr_2(s) + 1/2\ Br_2(g) \tag{12}$$

$$MoBr_3(s) + 1/2\ Br_2(g) \rightleftarrows MoBr_4(g) \tag{13}$$

Based on this example, one can formulate the course of the auto transport in general terms [25]: A compound $AB_x(s)$ does not generate a transport effective partial pressure of the gas species $AB_x(g)$ or $A(g)+B(g)$ $(AB(g)+B(g))$ on its own. The auto transport is based on two coexisting solid phases $AB_x(s)$ and $AB_{x-n}(s)$ as well as a gas phase which is generated through a decomposition reaction (14). The formed gaseous species $B$ then reacts under the formation of only gaseous product $AB_{x+n}$ in the sense of CVT reactions (15).
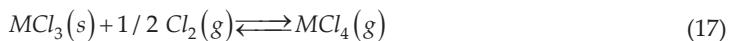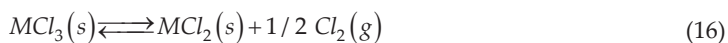
$$AB_x(s) \rightleftarrows AB_{x-n}(s) + nB(g) \tag{14}$$

**Figure 5.** Composition of the gas phase for the auto transport of MoBr$_3$.

$$AB_x(s) + nB(g) \rightleftharpoons AB_{x+n}(g) \tag{15}$$

Auto transports are generally endothermic reactions like sublimation and decomposition sublimation (deposition in the direction form source to sink: hot to cold). The transport equilibrium can only be effective if two conditions are met: First, the partial pressure of $B$ must be sufficiently high and second, the transporting phase $AB_x(s)$ must remain in equilibrium, thus $AB_x(s)$ must not be decomposed completely. $B$ stands for a gaseous decomposition product in the sense of equation (14). Thus, $B$ can be an atom (e.g. an bromine atom), a homonuclear molecule ($Cl_2$, $Br_2$, $O_2$,…) or a heteronuclear molecule.

There may be a smooth transition of the described phenomena of sublimation or decomposition sublimation to the mechanism of auto transport. The dissolution of $CrCl_3$ in the gas phase represents such a complex behavior. One can find congruent sublimation, the formation of gaseous chromium(III) chloride, and of an incongruent decomposition at the same time. In a consecutive reaction chlorine can react with the primary solid $CrCl_3$, thus becoming the transport agent. The transport effective gaseous molecule is $CrCl_4$, Figure 6. In case of the chlorides $MoCl_3$ or $VCl_3$, the gas molecules $MCl_3$ are too unstable or unknown and the movement in the temperature gradient takes place only through auto transport according to the equilibria (16) and (17) ($M$ = Cr, Mo, V).

$$MCl_3(s) \rightleftharpoons MCl_2(s) + 1/2\, Cl_2(g) \tag{16}$$

$$MCl_3(s) + 1/2\, Cl_2(g) \rightleftharpoons MCl_4(g) \tag{17}$$

The principle of auto transport is to apply also for other substance classes, such as oxides, chalcogenides and above all chalcogenide halides. As an example of the auto transport of an oxide, the crystallization of $IrO_2$ is presented. At temperatures of about 1050 °C the phase
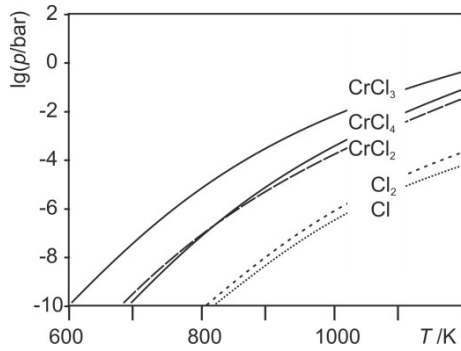
**Figure 6.** Composition of the gas phase for vapor transport processes of $CrCl_3$.

decomposes into the metal and molecular oxygen (18). In a subsequent heterogeneous equilibrium (19), oxygen reacts with the primary solid to form the transport effective gas species $IrO_3$, Figure 7. The back reaction takes place at lower temperature and $IrO_2$ is deposited.

$$IrO_2(s) \rightleftharpoons Ir(s) + O_2(g) \tag{18}$$

$$2IrO_2(s) + O_2(g) \rightleftharpoons 2IrO_3(g) \tag{19}$$
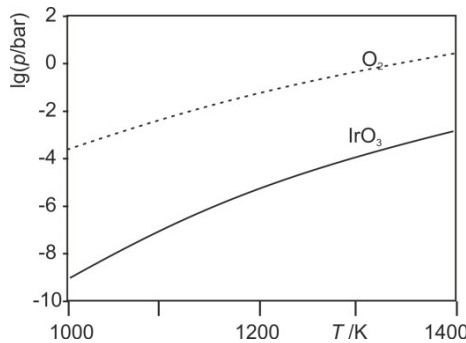


**Figure 7.** Composition of the gas phase for the auto transport of $IrO_2$.

Generally, all the auto transports are feasible as "regular" chemical vapor transport reactions. In these cases, the transport is possible as well through the addition of the transport agent without the preceding decomposition reaction. An important difference in both experiments can be observed: As the auto transport is based on a decomposition reaction, crystals of a different (metal rich) composition can be deposited. Thus the auto transport of $IrO_2$ leads to the deposition of $IrO_{2-x}$ (depleted by oxygen). Otherwise, the regular vapor transport in an

open systems oxygen stream ($p(O_2) = 1$ bar) leads to the formation of pure $IrO_2$ [1]. The transport behavior of $RuO_2$ is to discuss in the same way: by auto transport $RuO_{1.998}$ is obtained while $RuO_{2.0}$ crystallizes in vapor transport experiments with excess of oxygen [5]. Even if the change in composition is very small, the physical properties can differ significantly. Thus the specific electrical resistance of $RuO_2$ is of more than one order of magnitude higher than of $RuO_{2-x}$ [27].

If at least one of the components of $AB_x$ does not form a gas species with sufficient vapor pressure which is suitable for a substance transport (sublimation, decomposition sublimation, auto transport), the addition of an external transport agent will be necessary.

**Chemical Vapor transport reaction**: A chemical vapor transport reaction is characterized by the fact that another substance, the *transport agent*, is required for the dissolution of a solid in the gas phase. This characteristic is to illustrate by the example of vapor transport of zinc oxide by addition of chlorine. ZnO decomposes forming its own vapor phase with only small extent. Thus, the equilibrium pressure at a temperature of 1000 K is below $10^{-10}$ bar, Figure 8. By adding chlorine, the transport effective gas species $ZnCl_2$ and $O_2$ are formed in heterogeneous equilibrium (20). Here, the substances that appear in the vapor are different to those in the solid. Thereby transport effective vapor pressures ($p(i) > 10^{-4}$ bar) of the gas species can be observed already below 600 K, Figure 9.

$$ZnO(s) + Cl_2(g) \rightleftharpoons ZnCl_2(g) + 1/2 O_2(g) \tag{20}$$
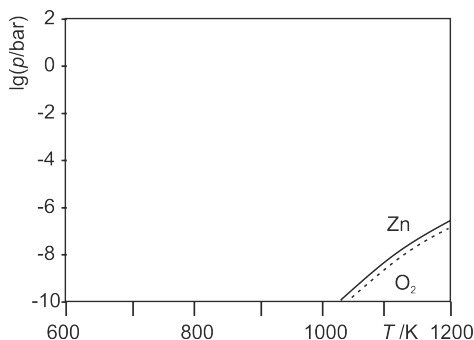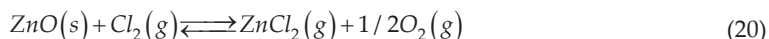


**Figure 8.** Composition of the gas phase for the thermal decomposition of ZnO.

The chemical vapor transport of ZnO is also possible by addition of hydrogen chloride. Likewise for the transport with chlorine $ZnCl_2$ is formed as the transport effective species for the transfer of zinc from source to sink, Figure 10. Otherwise the used transport agent HCl can react with oxygen, too. Thus the oxygen transferring species $H_2O$ is formed in equilibrium (21).

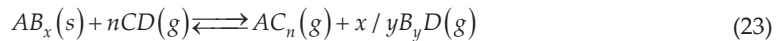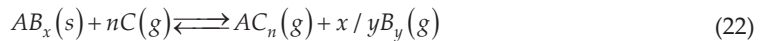$$ZnO(s) + 2HCl(g) \rightleftharpoons ZnCl_2(g) + H_2O(g) \tag{21}$$
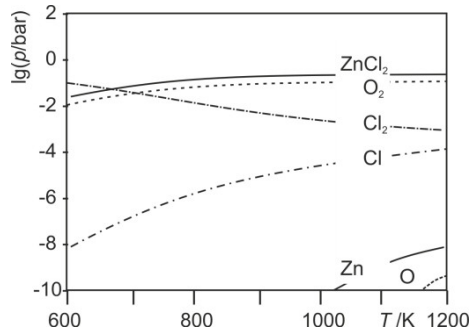
**Figure 9.** Composition of the gas phase for the CVT of ZnO with chlorine.
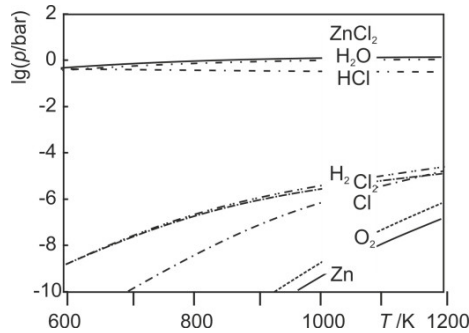


**Figure 10.** Gas phase composition for the CVT of ZnO with hydrogen chloride.

Here, the general principle of transport reactions can be seen clearly: The source material is transformed reversibly into gaseous products by the use of the transport agent. The transfer of the solid can be realized in different ways by formation of both heteronuclear species (like $ZnCl_2$ and $H_2O$) and atomar or homonuclear species ($O_2$).

$$AB_x(s) + nC(g) \rightleftharpoons AC_n(g) + x/yB_y(g) \tag{22}$$

$$AB_x(s) + nCD(g) \rightleftharpoons AC_n(g) + x/yB_yD(g) \tag{23}$$

## 2.2. Principles and thermodynamic considerations on CVT

In principle, two working methods are applied for the practical realization in the laboratory: the transport in open or closed systems. An open system is applied with an on both sides opened tube made of glass or ceramic material. Inside, a continuous flow of the transport agent is led over the source material; the solid, which is kept at a certain temperature, deposits at a

different place with another temperature under the release of the transport agent. In a closed system, typically a sealed ampoule, the transport agent remains in the system and constantly re-enters the reaction. Thus, in a closed system, a much smaller amount of the transport agent is needed. In some cases only few milligrams of the transport agent are sufficient to cause a transport effect. In the laboratory one predominantly works with closed systems. An easy closed system is a sealed glass tube. Such a *transport ampoule* has a typical length of 100 to 200 mm and a diameter of 10 to 20 mm. It includes about one gram of the solid which is to be transported, and as much transport agent as is needed to raise the pressure in the ampoule to one bar or less during the reaction.

It is of prime interest for preparative working chemists whether a certain solid can be prepared with the aid of chemical vapor transport reactions, which transport agents are suitable and under which conditions a transport can be expected. At this point, we want to appoint some general qualitative considerations.

- **The suitable transport agent for the investigated system**

The vapor transport reaction has to realize, that all formed products are gaseous under the reaction conditions. Thus a suitable transport agent is to select, which can transfer all components of the initial solid into the gas phase.

- **The basic precondition for successful CVT**

The equilibrium position of the transport reaction must not be extreme, so that dissolution into the gas phase and re-condensation of the solid are possible under slightly changed experimental conditions. In cases of an extreme equilibrium no dissolution occurs (evaporation reaction unfavored) or the formation of gaseous products is not reversible (back reaction under re-condensation unfavored). In both cases no vapor transport is observed.

- **The suitable temperature**

The temperature at which the numerical value of the equilibrium constant $K_p$ equals 1 ($\Delta_r G^0_T$ = 0) is referred to as optimal transport temperature $T_{opt}$ ($T_{opt} = \Delta_r H^0_T / \Delta_r S^0_T$).

- **The transport direction**

The transport is caused in almost every case by different temperatures and therefore changed equilibrium position in source and sink. It is common to characterize the volatilization (source) and the deposition temperature (sink) with $T_1$ and $T_2$, respectively, $T_1$ representing the lower temperature. The *transport direction* results from the sign of the reaction enthalpy of the transport reaction based on Le Chatelier's principle. Therefore, exothermic transport reactions always transport to the zone of higher temperature - from $T_1$ to $T_2$ ($T_1 \rightarrow T_2$), endothermic reactions transfer the solid to the cooler zone - from $T_2$ to $T_1$ ($T_2 \rightarrow T_1$).

- **The rate of mass transport**

A chemical vapor transport reaction can be divided into three steps: the *forward reaction* at the source material; the *gas motion*; and the *back reaction* leading to the formation of the solid in the crystallization zone. In most cases, the slowest and therefore the rate-determining step is the

gas motion. At a pressure of about 1 bar, the gas motion mainly takes place through diffusion; thus, the diffusion laws determine the velocity of the whole process. As we are observing the diffusion of gases, it is practicable to introduce the partial pressure gradient $dp/ds$. Thus, the transported amount of substance per time is proportional to the partial pressure gradient.

To intensify the theoretical understanding of chemical vapor transport reactions in a comprehensible way the representative experiment of the transport of tungsten(IV) oxide is illustrated. With the help of the clear example of the transport of $WO_2$, the mentioned general considerations can be tackled:

**The suitable transport agent for the investigated system.** The solid $WO_2$ does not have an own measurable vapor pressure which would be suitable to transfer the compound to the gas phase in the sense of a sublimation. The phase rather decomposes at 1000 K with an oxygen partial pressure of $10^{-20}$ bar towards metallic tungsten. Here, the addition of a transport agent is necessary. As a general rule, the halogens chlorine, bromine and iodine (24) or halogen compounds (25), such as the hydrogen halides $HX$ ($X$ = Cl, Br, I) are suitable as transport agents. For the transport of $WO_2$ the gas species $WO_2X_2$ can be effective for vapor transport. Thus all the components of the system – tungsten, oxygen, and chlorine – are present in the gas phase. Finally, the transport equations can reflect the formation of only gaseous species.

$$WO_2(s) + X_2(g) \rightleftharpoons WO_2X_2(g) \tag{24}$$

$$WO_2(s) + 2\,HX(g) \rightleftharpoons WO_2X_2(g) + H_2(g) \tag{25}$$
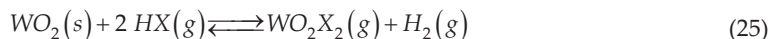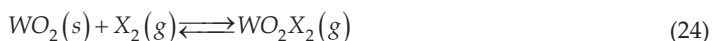
Also, adding mercury halides, which are solid at room temperature, is potentially suitable to transport both components of the solid phase – tungsten as well as oxygen – into the gas phase (26).

$$WO_2(s) + HgX_2(g) \rightleftharpoons WO_2X_2(g) + Hg(g) \tag{26}$$
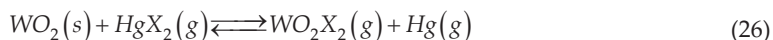
At temperatures above 300 °C the mercury halides evaporate completely. Afterwards the gas species $WO_2X_2$ is formed in addition to mercury. Here, only gaseous species ($WO_2X_2$(g)+Hg(g)) are formed, too.
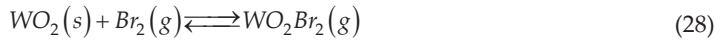
**The basic precondition for successful CVT.** Basic precondition for chemical vapor transport reactions is a balanced equilibrium position: For reactions which are described by *one* independent reaction equation, transports can be expected for equilibrium constants $K_p$ in the range from $10^{-4}$ up to $10^4$ respectively Gibbs energies $\Delta_r G^0$ of approx. −100 to +100 kJ mol$^{-1}$. The partial pressure gradient $\Delta p$ as a driving force for the material transport between dissolution and deposition site is achieved by a temperature gradient.

A highly exergonic reaction $\Delta_r G^0 < -100$ kJ mol$^{-1}$ ($K_p > 10^4$) shows a high dissolution of the solid into the gas phase. That sounds great. But: The back reaction under deposition of the solid phase is not possible in thermodynamic terms. That means that on the source side the trans-porting compound is almost completely transferred into the gas phase without depositing on the sink side. During a highly endergonic reaction $\Delta_r G^0 > 100$ kJ mol$^{-1}$ ($K_p < 10^{-4}$) the solid is hardly transferred into the gas phase, thus a transport cannot take place. With the help of thermodynamic data of the substances involved in the reaction, the values of the Gibbs energy, respectively the equilibrium constants of possible transport reactions can be calculated.
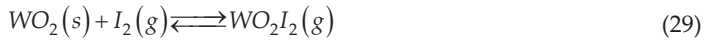
$$WO_2(s) + Cl_2(g) \rightleftharpoons WO_2Cl_2(g) \tag{27}$$
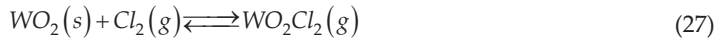
$\Delta_r H^0{}_{1000} = -86.5 \; kJ \cdot mol^{-1}, \; \Delta_r S^0{}_{1000} = 73.2 \; J \cdot mol^{-1} \cdot K^{-1}$

$\Delta_r G^0{}_{1000} = -159.7 \; kJ \cdot mol^{-1}, \; K_{p, \, 1000} \approx 10^8$

$$WO_2(s) + Br_2(g) \rightleftharpoons WO_2Br_2(g) \tag{28}$$

$\Delta_r H^0{}_{1000} = 13.0 \; kJ \cdot mol^{-1}, \; \Delta_r S^0{}_{1000} = 74.7 \; J \cdot mol^{-1} \cdot K^{-1}$

$\Delta_r G^0{}_{1000} = -61.7 \; kJ \cdot mol^{-1}, \; K_{p, \, 1000} \approx 10^3$

$$WO_2(s) + I_2(g) \rightleftharpoons WO_2I_2(g) \tag{29}$$

$\Delta_r H^0{}_{1000} = 112.4 \; kJ \cdot mol^{-1}, \; \Delta_r S^0{}_{1000} = 84.6 \; J \cdot mol^{-1} \cdot K^{-1}$

$\Delta_r G^0{}_{1000} = 27.8 \; kJ \cdot mol^{-1}, \; K_{p, \, 1000} \approx 10^{-2}$

$$WO_2(s) + 2 \, HCl(g) \rightleftharpoons WO_2Cl_2(g) + H_2(g) \tag{30}$$
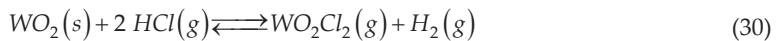
$\Delta_r H^0{}_{1000} = 31.0 \; kJ \cdot mol^{-1}, \; \Delta_r S^0{}_{1000} = 283.4 \; J \cdot mol^{-1} \cdot K^{-1}$

$\Delta_r G^0{}_{1000} = -252.4 \; kJ \cdot mol^{-1}, \; K_{p, \, 1000} \approx 10^{13}$

$$WO_2(s) + 2\, HBr(g) \rightleftharpoons WO_2Br_2(g) + H_2(g) \tag{31}$$
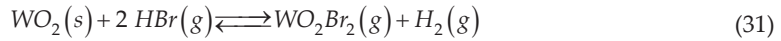
$\Delta_r H^0{}_{1000} = 105.7\ kJ \cdot mol^{-1},\ \Delta_r S^0{}_{1000} = 296.1\ J \cdot mol^{-1} \cdot K^{-1}$

$\Delta_r G^0{}_{1000} = -190.4\ kJ \cdot mol^{-1} K_{p,\,1000} \approx 10^{10}$

$$WO_2(s) + 2\, HI(g) \rightleftharpoons WO_2I_2(g) + H_2(g) \tag{32}$$
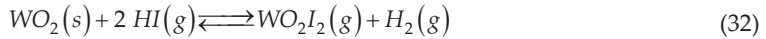
$\Delta_r H^0{}_{1000} = 174.6\ kJ \cdot mol^{-1},\ \Delta_r S^0{}_{1000} = 314.3\ J \cdot mol^{-1} \cdot K^{-1}$

$\Delta_r G^0{}_{1000} = -139.7\ kJ \cdot mol^{-1},\ K_{p,\,1000} \approx 10^{7}$
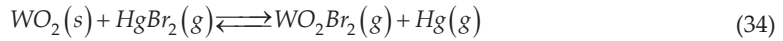
The calculations' results give a realistic outlook on the prospective results of transport experiments: Using halogens the transport with iodine seems to be promising (29). In the case of bromine, the transport seems at least possible (28) whereas chlorine causes an extreme equilibrium position under the formation of $WO_2Cl_2(g)$ – a transport should not be possible (27). With the hydrogen halides equilibria are far on the side of the reaction products (30 – 32). This is due to clearly higher gain of entropy during the reaction. Although one can observe gradations in the equilibrium position for transports with HI and HBr compared to HCl, transports are principally not expected.

The transport of $WO_2$ with mercury halides seems possible for all three transport agents $HgX_2$ ($X$ = Cl, Br, I): The equilibrium constants are within the limits of $10^{-4} < K_p < 10^4$. Thus, these systems are ideal to foster the understanding of a systematic approach and particularly to extend the understanding of chemical vapor transports. In the following, we shall focus on the transport of $WO_2$ with mercury halides. Using mercury bromide as a transport agent, the equilibrium position is least extreme (34) – in this case, the best transport results can be expected, see Figure 11. Using $HgCl_2(g)$ for the transport, the equilibrium position is shifted to the right (33); that means, the solid $WO_2$ is transferred well into the gas phase. However, the deposition of the solid on the sink side is only possible to a limited degree. Even when the temperature is decreased, the equilibrium position is still on the product side. The equilibrium constant for the transport with $HgI_2(g)$ indicates that the solid is hardly dissolved – the equilibrium position is shifted to the left (35). Thus, these are adverse conditions for a transport.

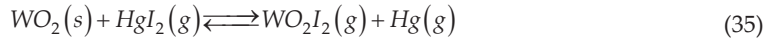$$WO_2(s) + HgCl_2(g) \rightleftharpoons WO_2Cl_2(g) + Hg(g) \tag{33}$$
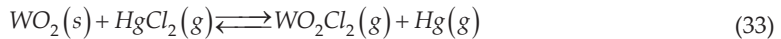
$\Delta_r H^0{}_{1000} = 115.5\ kJ \cdot mol^{-1},\ \Delta_r S^0{}_{1000} = 171.9\ J \cdot mol^{-1} \cdot K^{-1}$

$\Delta_r G^0{}_{1000}\ -56.4\ kJ \cdot mol^{-1},\ K_{p,\,1000} \approx 10^{3} bar$

$$WO_2(s) + HgBr_2(g) \rightleftharpoons WO_2Br_2(g) + Hg(g) \tag{34}$$

$\Delta_r H^0{}_{1000} = 190.5 kJ \cdot mol^{-1}$, $\Delta_r S^0{}_{1000} = 170.5 \ J \cdot mol^{-1} \cdot K^{-1}$

$\Delta_r G^0{}_{1000} = 20.0 \ kJ \cdot mol^{-1}$, $K_{p,\,1000} \approx 10^{-1} bar$

$$WO_2(s) + HgI_2(g) \rightleftharpoons WO_2I_2(g) + Hg(g) \tag{35}$$

$\Delta_r H^0{}_{1000} = 249.6 \ kJ \cdot mol^{-1}$, $\Delta_r S^0{}_{1000} = 179.2 \ J \cdot mol^{-1} \cdot K^{-1}$

$\Delta_r G^0{}_{1000} = 70.4 \ kJ \cdot mol^{-1}$, $K_{p,\,1000} \approx 10^{-4} bar$
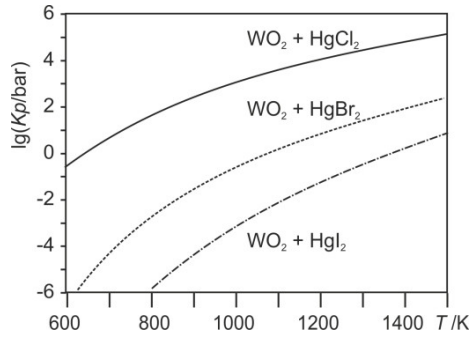


**Figure 11.** Equilibrium constants of transport reactions of $WO_2(s)$ with $HgX_2(g)$, $X$ = Cl, Br, I.

**The suitable temperature.** The optimum average temperature [$\bar{T} = (T_2+T_1)/2$] for chemical vapor transports results from the requirement of $\Delta_r G^0 \approx 0$. If the thermodynamic data of the reaction are known, which can easily be obtained from the values of the involved species according to Hess's law, the optimum average temperature can be calculated from quotient of the reaction enthalpy and entropy (38). Vant`t Hoff`s equation (37) establishes the link between the equilibrium constant $K$ and the thermodynamic data of the reaction enthalpy and entropy. The better the data, the more realistic are the results. With the help of standard data given for 298 K, the first estimation of the optimum transport temperature can be made. The results of this calculation are not to be met to the exact degree. One rather finds a range of ± 100 K which is suitable for the transport.

$$\Delta_r G_T^0 = - \Delta_r H_T^0 - T \cdot \Delta_r S_T^0 \tag{36}$$

$$\ln K = - \frac{\Delta_r H_T^0}{R \cdot T} + \frac{\Delta_r S_T^0}{R} \tag{37}$$

For the precondition of balanced equilibrium position at $K = 1$ ($\Delta_r G^0_T = 0$) results:

$$T_{opt} = \frac{\Delta_r H^0_T}{\Delta_r S^0_T} \tag{38}$$

Through differences in the temperatures of the source and sink side, the equilibrium position is brought towards the gaseous products when dissolving and shifted towards the solid when deposing. Calculations of the equilibrium constants were first made for an average temperature of 1000 K. If the temperatures vary, one will get the typical courses of the curve (see Figure 11). If the temperature is decreased, the equilibrium position in the transport system with $HgCl_2$ becomes less extreme. In contrast, the equilibrium position for the transport with $HgI_2$ becomes more favorable when the temperature is increased above 1000 K. The optimum, average temperature resulting from the quotient of the reaction enthalpy and entropy for the transport with $HgCl_2$ is at about 700 K respectively 400 °C; with $HgBr_2$ at about 1100 K respectively 800 °C and with $HgI_2$ 1400 K (1100 °C, respectively). In this case, the calculation of the temperature on the basis of the standard values at 298 K as well as of the derived values for 1000 K lead to the same results; which means that an estimation is possible with simple calculations, (39 – 41).

$$WO_2(s) + HgCl_2(g) \Longleftrightarrow WO_2Cl_2(g) + Hg(g) \tag{39}$$
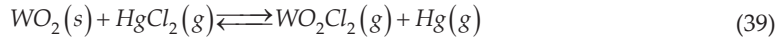
$\Delta_r H^0_{298} = 122.5 \; kJ \cdot mol^{-1}, \; \Delta_r S^0_{298} = 183.6 \; J \cdot mol^{-1} \cdot K^{-1}$

$T_{opt} = 125500 \; J \cdot mol^{-1} / 183.6 \; J \cdot mol^{-1} \cdot K^{-1}$

$T_{opt} \approx 700 \; K \; respectively \; 400 \; °C$

$$WO_2(s) + HgBr_2(g) \Longleftrightarrow WO_2Br_2(g) + Hg(g) \tag{40}$$
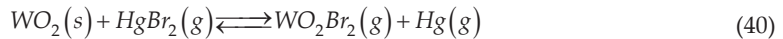
$\Delta_r H^0_{298} = 1881 \; kJ \cdot mol^{-1}, \; \Delta_r S^0_{298} = 170.0 \; J \cdot mol^{-1} \cdot K^{-1}$

$T_{opt} \approx 1100 \; K \; respectively \; 800 \; °C$

$$WO_2(s) + HgI_2(g) \Longleftrightarrow WO_2I_2(g) + Hg(g) \tag{41}$$
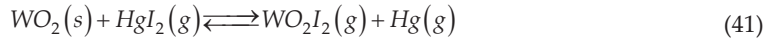
$\Delta_r H^0_{298} = 238.4 \; kJ \cdot mol^{-1}, \; \Delta_r S^0_{298} = 165.4 \; J \cdot mol^{-1} \cdot K^{-1}$

$T_{opt} \approx 1400 \; K \; respectively \; 1100 \; °C$

**The transport direction.** If a transport operation can be described in good approximation by only *one* reaction, the direction of the transport results from the heat balance of the heterogeneous equilibrium according to the van 't Hoff equation respectively to the Clausius–Clapeyron relation (42):

$$\frac{\mathrm{d}\ln K_p}{\mathrm{d}\frac{1}{T}} = -\frac{\Delta_r H_T^0}{R}$$

(42)

In a reaction with negative reaction enthalpy (exothermic dissolving reaction), the equilibrium constant $K_p$ increases with decreasing temperatures – thus dissolution takes place at low, deposition at high temperatures. To put it in other words: The transport is directed to the hotter zone ($T_1 \rightarrow T_2$).

$$\Delta_r H^0_T < 0; \; d \, lnK_p \sim \; d1/T$$

(43)

In a reaction with positive reaction enthalpy (endothermic dissolving reaction), $K_p$ increases with increasing temperatures – so dissolution takes place at higher, deposition at lower temperatures. Now, the transport proceeds to the cooler zone ($T_2 \rightarrow T_1$).

$$\Delta_r H^0_T > 0; \; d \, lnK_p \sim \; dT$$

(44)

The transport direction results only from the reaction enthalpy which is why the conclusion of all three investigated transport systems of $WO_2$ is clear: The reaction enthalpy is positive in each case – a transport to the cooler zone results. The total amount of the reaction enthalpy does not affect the decision if a transport is carried out. If the reaction enthalpy is close to zero one has to check the accuracy of the used data as they can contain errors of 10 to 20 kJ mol$^{-1}$.

**The rate of mass transport**. The substance transport via gas motion between dissolution and deposition site takes place by diffusion or convection. If the ampoule lies horizontally and if the total pressure is between $10^{-3}$ bar and 3 bar, the substance transport is affected by diffusion [1, 28]. In most cases, the diffusion is the velocity determining step, as it is much slower than the heterogeneous reaction of the solid with the transport agent. Using pressures above 3 bar, convection becomes dominating [28].

The term "*transport rate*" expresses the amount of deposited substance per time in the sink. For transports which run by only *one* reaction, one can describe the transport rate by Schäfer's transport equation (45) under the precondition that the chemical transport is solely determined by diffusion[1)] [1, 15]. High values of $\Delta p$ result in a high transport rate. A large cross section effects the transport rate positively as does a short transport distance. According to the transport equation a high average temperature is formally advantageous for the transport rate; however, the influence of the temperature on the equilibrium constant, and thus $\Delta p$ is more essential.

$$\dot{n}(A) = \frac{n(A)}{t'} = \frac{i}{j} \cdot \frac{\Delta p}{\Sigma p} \cdot \frac{\overline{T}^{0.75} \cdot q}{s} \cdot 0.6 \cdot 10^{-4} \left( mol \cdot l^{-1} \right) \tag{45}$$

$\dot{n}(A)$: Transport rate /mol h$^{-1}$

$i,j,k$ stoichiometric coefficients in transport equation: $i\,A$(s)+$k\,B$(g) = $j\,C$(g)+…

$\Delta p$: partial pressure difference of the *transport effective* species $C$ /bar

$\Sigma p$: total pressure /bar

$\overline{T}$ average temperature along the diffusion path /K (practically $\overline{T}$ results as an average of $T_1$ and $T_2$)

$q$: cross-section of the diffusion path /cm$^2$

$s$: length of the diffusion path /cm

$t'$ duration of the transport experiment /h

In most cases instead of the diffusion factor 0.6 10$^{-4}$ a value of 1.8 10$^{-4}$ is given which found entrance to the literature [1]. According to recent findings the factor 0.6 10$^{-4}$ results in a smaller numerical value of the diffusion coefficient and corrects a mathematical error.

The calculation of transport rates for WO$_2$ by Schornstein and Gruehn [29, 30] at first show a clear dominance of transports with HgBr$_2$ in the average temperature range: The expected transport rates are ten times higher than for transports with HgCl$_2$ and HgI$_2$. Due to the balanced position of the equilibrium, high differences of partial pressures occur between the source and the sink. This way, the driving force for diffusion of the gas particles is high and thus for the substance transport as well. For the transport with HgCl$_2$ the transport rate decreases with increasing temperatures. As we have already seen, the equilibrium position, which is far to the right side, is responsible for it. Only if the temperature decreases, the equilibrium position can move to the left. The resulting, higher differences of partial pressures between dissolution and deposition side cause increasing transport rates at low temperatures. Using mercury iodide as transport agent, the equilibrium position is on the side of the source material at low temperatures. By increasing the temperature the equilibrium position is shifted to the side of the reaction products, the transport rate increases, Figure 12.

Corresponding to the simple estimation of the transport behavior of WO$_2$ with mercury halides, one gets the best results with the addition of HgBr$_2$. The chemical vapor transport of mercury bromide is possible in a wide temperature range. Transport rates above 30 mg h$^{-1}$ are achievable, Figure 13. Temperatures of the source side of about 800 °C and of the sink side of 720 °C prove optimum. This result confirms the estimations of the optimum transport temperature. Due to the shift of the equilibrium position, the transport rate decreases at both, rising temperatures (880 → 800 °C respectively 960 → 880 °C; and falling temperatures (720 → 640 °C) [2]. Transports with HgCl$_2$ and HgI$_2$ clearly show smaller transport rates. Experiments with mercury iodides must be realized with higher temperatures according to the estimation. Temperatures up to 1000 °C are practicable; above, the silica glass ampoule will be heavily damaged by re-crystallization. Using an average transport temperature of 940 °C, transport
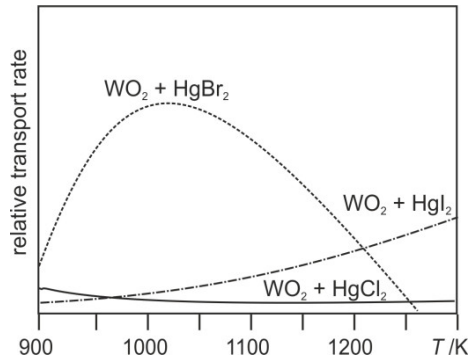
**Figure 12.** Progression of theoretical transport rates during the transport of $WO_2$ with $HgX_2$ ($X$ = Cl, Br, I) according to [29, 30].

rates of up to 15 mg h$^{-1}$ can be achieved, Figure 13. The transport rate decreases drastically with falling temperatures. With an average temperature of 640 °C the rate is even lower than 1 mg h$^{-1}$. Transport experiments with $HgCl_2$ show worst results as far as the transport rate is concerned: According to the calculation, lower temperatures are principally more favorable, however, in the range from 500 to 700 °C the transport rates are only in the range of 1 mg h$^{-1}$. The transport almost grinds to a halt at higher temperatures.
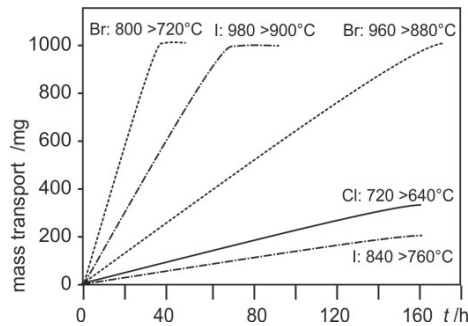


**Figure 13.** Experimental transport rates during the transport of $WO_2$ with $HgX_2$ ($X$ = Cl, Br, I) according to [2].

One can come to a completely different evaluation if the quality of the crystals instead of the transport rate is given prominence. Relatively high transport rates cause uncontrolled nucleation and crystal growth. As a consequence, one gets highly epitaxial and rose-shaped crystal agglomerations for transports with $HgBr_2$. Frequently *one* compact solid of these epitaxial crystallites of $WO_2$ is found in the sink. Using average temperatures of approx. 800 °C in the transport system with $HgI_2$, one gets isolated, rod-shaped crystals of up to 1 mm edge length, Figure 14. The preparation of mono-crystals for crystal structure analysis is possible from these approaches, even though not every crystal is suitable. The low transport rate of 1

to 2 mg h$^{-1}$ makes an undisturbed nucleation and crystal growth possible in this case. In the process, smaller, highly defected crystallites are dissolved in favor of other individuals.
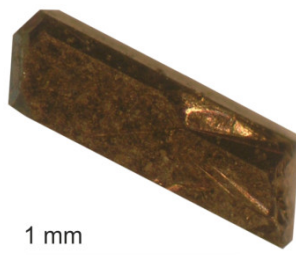


**Figure 14.** Typical crystal morphology of single crystallites formed during the transport of WO$_2$ with HgI$_2$.

Finally, in selecting the transport agent, the temperature, and the temperature gradient, respectively, one should consider the aim of the transport. A high transport rate is undoubtedly advantageous for the synthesis of a compound or the purification of it. If crystals are to be grown, keep in mind the crystal quality and therefore rather choose a smaller transport rate.

**Conclusion**. Chemical vapor transport reactions are predictable. Simple estimations concerning the feasibility and the course of transport reactions are already possible with a basic understanding of the method and its thermodynamic backgrounds. It is worth the effort in every case – one avoids unnecessary experiments using "trial and error" procedure. Conclusions by analogy between similar transport systems are helpful as a first guide. However, the factual favorable parameter for a transport system should be estimated carefully in advance

# 3. Chemical vapor transport reactions – applications

## 3.1. Transport agents and gas species

It is of prime interest for preparative working chemists whether a certain solid can be prepared by chemical transport reactions, which transport agents are suitable and under which conditions a transport can be expected. If one wants to use transport reactions only in a preparative way – without the purpose of understanding the course of the reaction in detail – often it is sufficing to check on an empiric basis which solid can be transported by using what kind of transport agent. A further, quantitative description of the transport reaction requires knowledge of the thermodynamic data of the condensed phases and gaseous molecules that are involved. In this section, we will provide a short overview of the different kinds of gaseous inorganic molecule that can occur during chemical vapor transport reactions. Under the precondition of formation of only gaseous species, transport agents and transport effective species share the property of high volatility under experimental conditions. Thus, especially

halogens and halogen compounds are qualified. Some elements, hydrogen compounds, and oxygen compounds are suitable as transportable species, too.
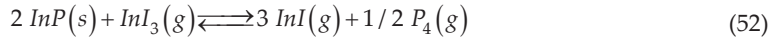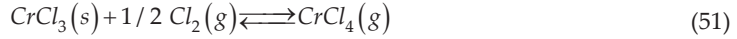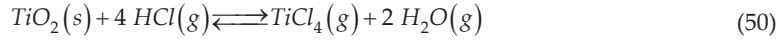
**Halogen compounds**. Due to its volatility, metal halides and non-metal halides play a central role for chemical transport reactions. Thus, halogens and many halogen compounds are effective and often used transport agents.

**Halogens and halogen compounds as transport agents**. The elemental halogens chlorine, bromine and iodine are used frequently as transport agent. Fluorine, in contrast, is not suited due to extreme equilibrium position of formation of fluorides in most cases. Besides, there are material problems because fluorine reacts with the ampoule materials if silica glass is used. Under the pertinent transport conditions, chlorine, bromine, and iodine react with solids of different substance classes, e.g. with metal, intermetallic compounds, semi-metals, metal oxides, sulfides, selenides, tellurides, nitrides, phosphides, arsenides, antimonides, silicides, germanides, some metal halogens and more. In the process, gaseous metal halides respectively semi-metal halides and the respective non-metal are formed as a rule. In some cases, non-metal halides are formed. Thus, during a reaction of metal phosphides with a halogen or a halogen compound, not only metal halides but also phosphoric halides can occur. Due to the fact that halides show oxidizing characteristics, metal halides or oxide halides are often formed as transport effective species in which the metal has a higher oxidation level than in the solid as shown for the transport of chromium(III) chloride with chlorine (46) or tungsten(IV) oxide with iodine (47).

$$CrCl_3(s) + 1/2\ Cl_2(g) \rightleftharpoons CrCl_4(g) \tag{46}$$

$$WO_2(s) + I_2(g) \rightleftharpoons WO_2I_2(g) \tag{47}$$
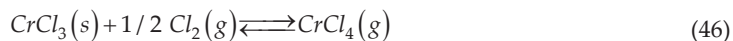
Hydrogen halides are versatile transport agents. The oxidation levels of the metal in the solid and in the transport effective gas species are generally equal because hydrogen halides do not have an oxidizing effect. Hydrogen halides are often used during the transport of oxides. Here, the gaseous metal halide and water vapor are formed. Halogen compounds, such as $TeCl_4$, $PCl_5$, $NbCl_5$ or $TaCl_5$ are also useful transport agents, especially for metal oxides. Reactions of the mentioned chlorides lead on the one hand to the formation of gaseous metal chloride or metal oxide chloride, on the other hand oxygen is fixed in form of volatile oxides ($TeO_2$, $P_4O_6$, $P_4O_{10}$) or oxide chlorides ($TeOCl_2$, $POCl_3$, $NbOCl_3$, $TaOCl_3$). Oppermann was able to show that tellurium(IV) chloride is a particular versatile transport agent [31]. According to the basic works of Schäfer, gaseous metal respectively semi-metal halides are formed as transport effective species during the reaction of different solids with halogens or halogen compounds [1].
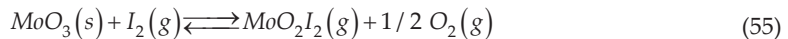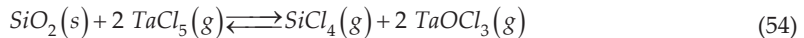
$$Co(s) + I_2(g) \rightleftharpoons CoI_2(g) \tag{48}$$

$$Si(s) + SiI_4(g) \rightleftharpoons 2\ SiI_2(g) \tag{49}$$

$$TiO_2(s) + 4\ HCl(g) \rightleftharpoons TiCl_4(g) + 2\ H_2O(g) \tag{50}$$

$$CrCl_3(s) + 1/2\ Cl_2(g) \rightleftharpoons CrCl_4(g) \tag{51}$$

$$2\ InP(s) + InI_3(g) \rightleftharpoons 3\ InI(g) + 1/2\ P_4(g) \tag{52}$$

The vapor of metal halides can consist of monomeric, dimeric and/or oligomeric molecules. With $M$ = Al, Ga, In, Fe, Sc, Y, $Ln$ ($Ln$ = lanthanoides), one can observe particular large amounts of dimers $M_2X_6$. Trimers occur with copper(I) halides and silver halides. Metal halides of different components $A$ and $B$ can react in the gaseous state under the formation of *gas complexes* [32]. Such gas complexes are also formed during heterogeneous reactions between solid and gaseous halides. For example, gaseous aluminum(III) chloride reacts with a number of heavy volatile, solid metal chlorides under the formation of gas complexes. This way, their volatility is massively increased, often by orders of magnitude. These reactions can be used in vapor transport experiments [33]. This way, cobalt chloride can be transported with aluminum(III) chloride (53) far below the boiling temperature (e.g. 400 → 350 °C) [34]. To date, numerous of these examples are known [34 - 37]. Thermodynamic data were determined for a considerable number of gas complexes [38] and empirical rules which can help estimating the thermodynamic data of gas complexes are laid down [36, 38].

$$CoCl_2(s) + Al_2Cl_6(g) \rightleftharpoons CoAl_2Cl_8(g) \tag{53}$$
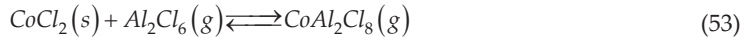
**Oxide halides**. Gaseous oxide halides are known of few metals only, in particular of transition elements [39]. These molecules appear in particular in case of metals with high oxidation numbers. $VOX_3$, $NbOX_3$, $TaOX_3$ ($X$ = F…I), $CrO_2X_2$ ($X$ = F…Br), $MoO_2X_2$, $WO_2X_2$ ($X$ = F…I), $MoOX_4$, $WOX_4$ ($X$ = F…Br), $ReOCl_4$, $OsO_2Cl_2$, $OsOCl_4$, $RuOCl$, $ReO_3X$ ($X$ = F…I). Gaseous oxide halides can play an important part as transport effective species during the transport of oxides [40].

$$SiO_2(s) + 2\ TaCl_5(g) \rightleftharpoons SiCl_4(g) + 2\ TaOCl_3(g) \tag{54}$$

$$MoO_3(s) + I_2(g) \rightleftharpoons MoO_2I_2(g) + 1/2\ O_2(g) \tag{55}$$

Some gaseous oxide halides are known of main group metals. Elements of group 13 form oxide halides, such as AlOCl, at very high temperatures around 2000 °C. Phosphorus forms several oxide chlorides and -bromides that are stable at high temperatures: $POX_3$, $PO_2X$, and $POX$ ($X$ = Cl, Br) [42]. For arsenic and antimony AsOCl and SbOCl are stable at high temperatures, however, oxide halides with the metal in the oxidation stage V are not known [42]. $TeOCl_2$ is the most important oxide halide of the main group elements. This gas species plays an important role during the transport of numerous oxides with tellurium(IV) chloride [31].
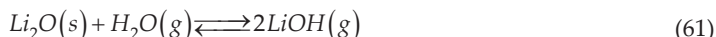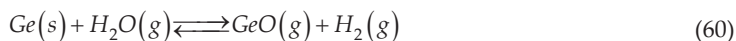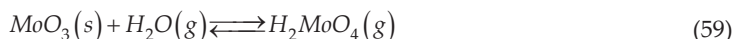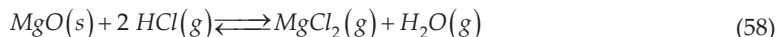
**Elements in gaseous state**. The importance of elemental halogens for chemical vapor transport reactions was already mentioned. Other elements also often occur in gaseous state during transport reactions, especially gaseous non-metals. Gaseous species of elements of groups 15 and 16 are formed during the transport of pnictides or chalcogenides with halogens (56) or halogen compounds in many cases. In contrast, metal gas species play a role in only a few reactions. In particular, this behavior occurs, if the transport agent reacts with the non-metal instead of the metal atoms and the metal is sufficient volatile (57). The formation of an unsaturated metal vapor during transport reactions can only be expected if the boiling temperature of the metal is below approx. 1200 °C. This only applies to the following metals: Na (881 °C), K (763 °C), Rb (697 °C), Cs (657 °C), Mg (1093 °C), Zn (906 °C), Cd (766 °C), Hg (356 °C), Yb (1194 °C) and Te (989 °C).

$$ZrAs_2(s) + 2\ I_2(g) \Longleftrightarrow ZrI_4(g) + 1/2\ As_4(g) \tag{56}$$

$$ZnO(s) + H_2(g) \Longleftrightarrow Zn(g) + H_2O(g) \tag{57}$$
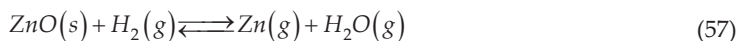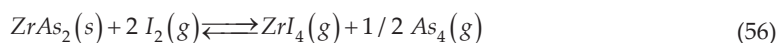
In some cases, gaseous elements can work as transport agents. Hence, oxygen can cause the transport of some platinum metals [40]. Sulfur can transport a series of transition metal sulfides [43]. Here, gaseous polysulfides, such as $TaS_3$, are assumed transport effective species. There are similar observations for the chemical transport of some selenides. Sulfur is an effective transport agent for tellurium as well [44]. Compounds in which tellurium atoms were integrated in the different ring-shaped sulfur molecules were detected as transport effective species. Phosphorus can transport gallium phosphide, GaP, and indium phosphide, InP, probably via $GaP_5$ respectively $InP_5$ as transport effective species [45]. With the help of arsenic, the transport of gallium arsenide, GaAs, and indium arsenide, InAs, succeeded in a similar way [46].

Metal vapors predominantly consist of the atoms. The fraction of bi- or polyatomic molecules in the saturated vapor is between $10^{-5}$ and 10 % [47]. In contrast, the vapors of non-metals, apart from noble gases, consist of very stable polyatomic molecules which appear in the gas phase in great amounts, atoms appear only subordinated: $N_2$, $P_4$, $P_2$, $As_4$, $As_2$, $Sb_4$, $Sb_2$, $O_2$, $S_2$, $S_3 \ldots S_7$, $S_8$, $Se_2$, $Se_3 \ldots Se_7$, $Se_8$, $Te_2$, $Cl_2$, $Br_2$, and $I_2$. The ratio of different molecular species in the vapors of non-metals depends on the temperature and the pressure. Higher temperature and lower pressures abet the formation of small molecules respectively atoms.

**Hydrogen compounds**. Hydrogen compounds of non-metals play an important role for chemical vapor transport reactions. Hydrogen halides, which are often used as transport agents, are particularly important; for example during the transport of metal oxides. The example (58) shows that water vapor becomes transport effective species. However, water can also function as transport agent as for the transport of molybdenum(VI) oxide (59) and the one of germanium (60). Additionally, water can lead to the formation of transport effective gaseous hydroxides (61):

$$MgO(s) + 2\,HCl(g) \rightleftharpoons MgCl_2(g) + H_2O(g) \tag{58}$$

$$MoO_3(s) + H_2O(g) \rightleftharpoons H_2MoO_4(g) \tag{59}$$

$$Ge(s) + H_2O(g) \rightleftharpoons GeO(g) + H_2(g) \tag{60}$$

$$Li_2O(s) + H_2O(g) \rightleftharpoons 2LiOH(g) \tag{61}$$

The transport reaction of tungsten with water and iodine is an important one in daily life. This reaction provides the basis of the operating mode of halogen lamps.

$$W(s) + 2\,H_2O(g) + 3\,I_2(g) \rightleftharpoons WO_2I_2(g) + 4\,HI(g) \tag{62}$$
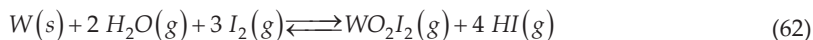
Traces of water, often from the wall of the silica glass tubes, which were used during the transport, can be important for transport effects [48]. Hydrogen sulfide and hydrogen selenide also appear during the transport of sulfides respectively selenides with hydrogen halides. Hydrogen telluride is too unstable to develop under transport conditions. Ammonium chloride is particularly important. It decomposes to ammonia and hydrogen chloride during sublimation. Thus, it is a hydrogen chloride source which is easy to handle and easy to dose. Ammonia decomposes to the elements at higher temperature and thus creates a reducing atmosphere which effects the equilibria involved in the transport in different ways.

**Oxygen compounds**. The large amount of metal oxides decomposes completely or partly while heating to high temperatures. Gingerich provides a compilation of gaseous metal oxides and their stability [47]. Some metal oxides vaporize congruently: $CrO_3$, $MoO_3$, $WO_3$, $Re_2O_7$, $IrO_3$, $RuO_3$, $RuO_4$, $OsO_4$, $GeO$, $SnO$, and $PbO$. In the vapors of $CrO_3$, $MoO_3$ and $WO_3$ trimeric molecules appear as $M_3O_9$. $SnO$ and $PbO$ form dimers and trimers. Nevertheless, gaseous metal oxides play a subordinated role for chemical vapor transport reactions [40, 49]:

$$OsO_2(s) + OsO_4(g) \rightleftharpoons 2\ OsO_3(g) \tag{63}$$

$$Pt(s) + O_2(g) \rightleftharpoons PtO_2(g) \tag{64}$$
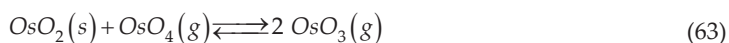
The role of non-metals is more important. Carbon monoxide can function as transport agent in different ways [50]:
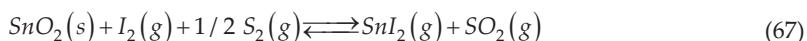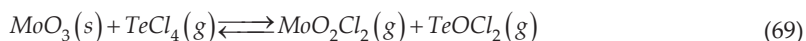
$$SnO_2(s) + CO(g) \rightleftharpoons SnO(g) + CO_2(g) \tag{65}$$

$$Ni(s) + 4\ CO(g) \rightleftharpoons Ni(CO)_4(g) \tag{66}$$
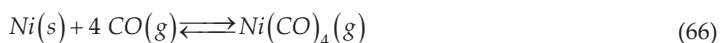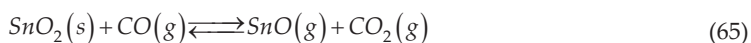
Non-metal oxides occur as *transport effective species* for the transport of oxides. Thus, sulfuric vapor can cause in presence of iodine the transport of tin(IV) oxide [51].

$$SnO_2(s) + I_2(g) + 1/2\ S_2(g) \rightleftharpoons SnI_2(g) + SO_2(g) \tag{67}$$

During the chemical transport of metal oxides, tellurium(IV) chloride plays a particular role, it reacts under the formation of a metal chloride or a metal oxide chloride and binds oxygen in form of $TeO_2(g)$ or $TeOCl_2(g)$ at the same time [31].

$$TiO_2(s) + TeCl_4(g) \rightleftharpoons TiCl_4(g) + TeO_2(g) \tag{68}$$

$$MoO_3(s) + TeCl_4(g) \rightleftharpoons MoO_2Cl_2(g) + TeOCl_2(g) \tag{69}$$

Further gaseous oxides that are important for the transport of oxide compounds are amongst others: $B_2O_3$, SiO, $P_4O_6$, $P_4O_{10}$, $As_4O_6$, $Sb_4O_6$, $SeO_2$.

**Other substance groups**. During some transport reactions, gaseous sulfides, selenides, tellurides or sulfide halides are of particular importance. Thus, boron can be volatilized in presence of sulfur or selenium; In this context, the molecules $BS_2$ [52] and $BSe_2$ [53] were detected. Aluminum also forms gaseous sulfides and selenides at high temperatures: $Al_2S$, AlS, $Al_2S_2$, $Al_2Se$, AlSe, $Al_2Se_2$ [54]. Gaseous sulfides, selenides and tellurides of group 14 are also known: SiS, SiSe, SiTe, GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbS, PbSe, PbTe [54]. These molecules form dimers to a minor degree. Disulfides respectively diselenides of these elements are less stable. The gaseous monosulfide, PS, of sulfur is described [55].

Gaseous sulfide halides or selenide halides are known of only a few elements. For example, PS$X_3$ and PS$X$ ($X$ = F, Cl, Br) [42] for phosphorus are described. Niobium forms the gaseous sulfide halides respectively selenide halides NbSCl$_3$, NbSBr$_3$, NbSeBr$_3$ [56], for tantalum TaSCl$_3$ and TaSeBr$_3$ are known [56]; the transport effectiveness of MoSBr was mentioned [57]. Tungsten forms two volatile sulfide chlorides, WS$_2$Cl$_2$ [39] and WSCl$_4$ [58]. The thermodynamic data of WS$_2$X$_2$ ($X$ = Cl, Br, I) were determined [59]. The transport effectiveness of the hydrated oxide halides, Bi(OH)$_2$X ($X$ = Cl, Br, I), was reported [60]. Finally, Pt(CO)$_2$Cl$_2$ is a gaseous compound that becomes transport effective during the transport of platinum with carbon monoxide and chlorine [61].

## 3.2. Chemical vapor transport of elements and compounds

To date the chemical vapor transport of almost all substance classes has been described. This chapter will show characteristic examples of different transport reactions. A comprehensive overview with more than 2000 references of CVT is not intended here. For more details and references of CVT of elements and compounds see [2]. The chemical vapor transport of elements has been studied and described in detail using metals and some semi-metals as examples; the transport of intermetallic phases principally follows the one of metals. The oxides are the largest group among all compounds which were crystallized by chemical transport reactions with more than 600 examples. The transport of chalcogenides clearly differs from the ones of the oxides. This is due to the higher thermodynamic stability of the metal oxides, compared to the sulfides, selenides, and tellurides. Finally, the chemical vapor transport provides a very good access to phosphides and arsenides, too.

### 3.2.1. Chemical vapor transport of elements

The chemical transport of elements has been studied and described in detail using metals and some semi-metals as examples. In the case of the typical non-metals phosphorus and sulfur, there is no need to increase their volatility in the sense of a chemical vapor transport reaction due to their high vapor pressures. This way, those metals and semi-metals which feature high vapor pressures can also easily be transferred into the gas phase through distillation or sublimation. The following elements belong to this group: Alkali and alkaline earth metals, zinc, cadmium, mercury, europium, ytterbium, arsenic, antimony, selenium and tellurium. Some metals' melting temperature is that low that they can be obtained in liquid form at the most. This, for example, applies for gallium, tin and lead. Thus, chemical vapor transports are relevant for high melting elements with low vapor pressures. These elements can be deposited from the gas phase in closed reaction vessels (ampoules), fluid systems, special reactors (hot-wire process according to (Van Arkel und De Boer), or through CVD-processes [62]. All of these processes are based on the same thermodynamic basic principles. This way, more than 40 elements can be crystallized with chemical transport reactions, more than 25 with iodine as transport agent [63, 64].

In addition to iodine as most important transport agent for elements, compounds such as aluminum(III) chloride, gallium(III) chloride and iron(III) chloride as well as aluminum(III) iodide and indium(III) iodide are described as transport effective additive [65]. These can act

halogenating and thus form gaseous halides with the transporting elements. Additionally, they stabilize them by forming gaseous complexes. Halogens such as fluorine, chlorine and bromine as well as the hydrogen halides, water, the chalcogens oxygen, sulfur, selenium, tellurium as well as carbon monoxide are other transport agents which can be used in individual cases. Although carbon monoxide can be used for the transport of nickel only, the industrial purifying process according to Mond and Langer found its way into chemistry textbooks, making carbon monoxide particularly prominent as a transport agent [66]. More details and references of CVT of the elements are presented in [2].

**Iodine as transport agent**. The exothermic transport of an element with iodine from $T_1$ to $T_2$ is the most frequently described transport reaction involving metals. This reaction type were studied and described extensively for titanium, zirconium, hafnium, and thorium (process of van Arkel and de Boer) [67 -70]. Further elements which can be transported this way are yttrium, vanadium, niobium, tantalum, chromium, iron, cobalt, nickel, copper, boron, silicon, germanium and tin as well as uranium and protactinium [63, 64, 71 - 75]. This kind of transport to the hotter zone shall be illustrated with the example of the transport of zirconium with iodine. The temperatures of the dissolving side $T_1$ can vary between 200 and 650 °C. The most suitable temperature is between 350 and 400 °C. The temperatures of the decomposing side $T_2$ can be between 1100 and 2000 °C; whereby temperatures around 1400 °C are usually applied. Often, a wire heated by current flow is the place of decomposition. The transport behavior is described by the equilibria (70 – 72), Figure 15.
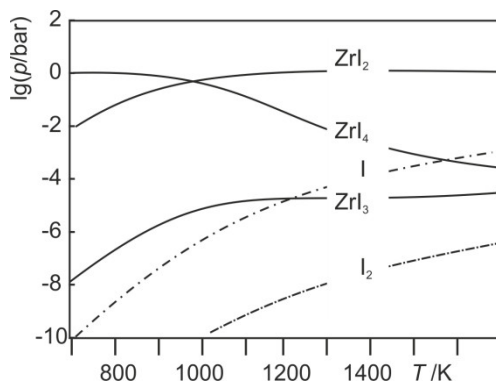


**Figure 15.** Partial pressures of species in the transport system Zr/I.

$$Zr(s) + 2\,I_2(g) \rightleftharpoons ZrI_4(g) \tag{70}$$

$$Zr(s) + I_2(g) \rightleftharpoons ZrI_2(g) \tag{71}$$

$$I_2(g) \rightleftharpoons 2\,I(g) \tag{72}$$

According to Van Arkel, iron can be transported exothermically with iodine from 800 to 1000 °C. At first, the following transport equation (73) comes into consideration. This reaction, however, is endothermic. According to Le Chatelier's principle, transport from $T_2$ to $T_1$ is expected. Because of the strict validity of this principle, one has to assume that the transport obviously cannot be described, or at least not alone, by the reaction formulated above. A detailed investigation showed that other reactions take place as well. Accordingly, iron(II) iodide forms monomer and dimer molecules, $FeI_2$ and $Fe_2I_4$, in the vapor. The reaction of iron and iodine with the formation of gaseous $Fe_2I_4$ molecules (74) can be described. This reaction equation has the character of a transport equation, too. As the reaction (74) is exothermic, one expects transport from $T_1$ to $T_2$.

$$Fe(s) + I_2(g) \rightleftharpoons FeI_2(g) \tag{73}$$

$\Delta_r H^0_{298} = 24\ kJ \cdot mol^{-1}$

$$2\,Fe(s) + 2\,I_2(g) \rightleftharpoons Fe_2I_4(g) \tag{74}$$

$\Delta_r H^0_{298} = -116\ kJ \cdot mol^{-1}$

Using the example of the transport of germanium with iodine, Oppermann and colleagues investigated the proportion of diffusion and convection of the gas movement at different total pressures. In comparative experiments, the transport behavior was determined at normal gravity on earth and under microgravity in space [28]. At microgravity conditions, the convection is negligibly small; substance transport takes place by diffusion only. The experiments indicated that in the gravitational field of earth the gas movement above 3 bar occurs not only by diffusion, but increasingly by convection.
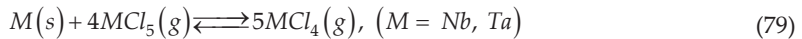
The knowledge gained for exothermic transports with iodine also applies for the other halogens. However, their meaning as transport agents for elements is of low importance due to their unsuitable equilibrium situation. Because the stability of halides increases from iodides to fluorides, their decompositions temperatures increase as well in that direction. Higher decomposition temperatures become necessary which are more difficult to put into practice in experiments.

**Conproportionation reactions**. Besides the formation and decomposition of the halides, also conproportionation reactions (dissolution) respectively disproportionation (deposition) can be used for the chemical transport of elements. During such reactions, at least two halides of different composition appear in the gas phase (75).

$$Si(s) + SiX_4(g) \rightleftharpoons 2\ SiX_2(g) \tag{75}$$

$(X = F,\ Cl,\ Br,\ I,\ 1100 \rightarrow 900\,^\circ C)$

The increase of entropy is the driving force of the endothermic formation of the low halide. The transport always takes place from $T_2$ to $T_1$. Elements which can be transported by these reactions are amongst others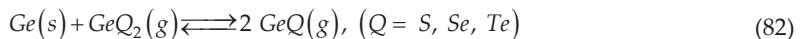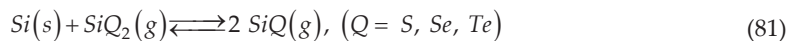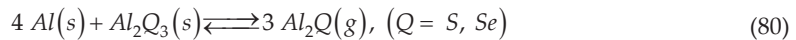 beryllium, zinc, cadmium, boron, aluminum, gallium, silicon, germanium, tin, antimony and bismuth [8]. The according halides can directly be used as transport agent. Instead the halogen is added in many cases. In this process, the halides are formed by a primary reaction. The given examples can be generalized as follows:

$$M(s) + MX_2(g) \rightleftharpoons 2MX(g),\ \left(M =\ Be,\ Cd,\ Zn\right) \tag{76}$$

$$2M(s) + MX_3(g) \rightleftharpoons 3MX(g),\ \left(M =\ B,\ Al,\ Ga,\ In,\ Sb,\ Bi\right) \tag{77}$$

$$M(s) + MX_4(g) \rightleftharpoons 2MX_2(g),\ \left(M =\ Si,\ Ge\right) \tag{78}$$

$$M(s) + 4MCl_5(g) \rightleftharpoons 5MCl_4(g),\ \left(M =\ Nb,\ Ta\right) \tag{79}$$
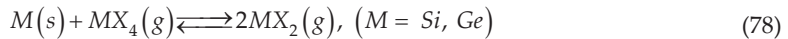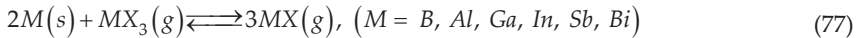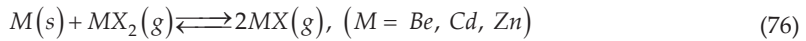
The principle of conproportionation can also be used for transport reactions with chalcogenides [76] as shown by the following examples:

$$4\ Al(s) + Al_2Q_3(s) \rightleftharpoons 3\ Al_2Q(g),\ \left(Q =\ S,\ Se\right) \tag{80}$$

$$Si(s) + SiQ_2(g) \rightleftharpoons 2\ SiQ(g),\ \left(Q =\ S,\ Se,\ Te\right) \tag{81}$$

$$Ge(s) + GeQ_2(g) \rightleftharpoons 2\ GeQ(g),\ \left(Q =\ S,\ Se,\ Te\right) \tag{82}$$

**Reversal of the transport direction**. If several reactions are necessary in order to describe the transport of an element respectively a solid, endothermic and exothermic reactions can be relevant. Which of these reactions is the dominant and thus the direction determining one is dependent on the total pressure and the temperature. Thermodynamic discussion shows that

the transport direction can be reversible if the transport conditions are varied. There is a change of the transport direction during the deposition of titanium when iodine is added. At lower temperature (< 1000 °C), the endothermic equilibrium (83) predominates while the transport at higher temperatures is determined by the exothermic equilibrium (84).
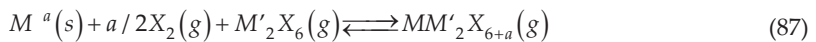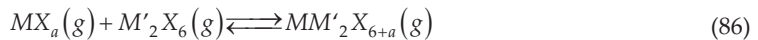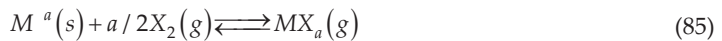
$$Ti(s) + TiI_4(g) \rightleftharpoons 2\ TiI_2(g) \tag{83}$$

$\Delta_r H^0{}_{298} = 237.9\ kJ \cdot mol^{-1}$

$$Ti(s) + 4\ I(g) \rightleftharpoons TiI_4(g) \tag{84}$$

$\Delta_r H^0{}_{298} = -704.3\ kJ \cdot mol^{-1}$

**Formation of gas complexes**. Besides pure halogenating equilibria, halogenating equilibria in combination with complex formation equilibria are of importance for the chemical transport of elements [65]. In the process, the formation of gas complexes leads to an increase of the solubility of the respective element in the gas phase. $AlX_3$, $GaX_3$, $InX_3$ and $FeX_3$ ($X$ = Cl, Br, I) are used as complexing agents whereby the chlorides are used most often. In the gas phase, the mentioned halides can be present as dimeric molecules to a considerable extent. Amongst others, silver, gold, cobalt, chromium, copper, nickel osmium palladium, platinum, rhodium and ruthenium can be transported via complex formation equilibria. In many cases, in particular at temperatures below 500 °C, the transport effective equilibria can be generally described by the following equations. The transport equation is the sum of the equilibria (85) and (86). The formation of gas complexes according to (87) is always endothermic.

$$M^a(s) + a/2X_2(g) \rightleftharpoons MX_a(g) \tag{85}$$

$$MX_a(g) + M'_2X_6(g) \rightleftharpoons MM'_2X_{6+a}(g) \tag{86}$$

$$M^a(s) + a/2X_2(g) + M'_2X_6(g) \rightleftharpoons MM'_2X_{6+a}(g) \tag{87}$$

($M$ = Co, Cu, Ni, Pd, Pt, $M'$ = Al, Ga, In, Fe, $X$ = Cl, Br, I)
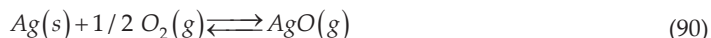
**Transport with addition of hydrogen halides and water**. As far as the transport of metals is concerned, the hydrogen halides are of minor importance. Only chromium, iron, cobalt, nickel and copper can be endothermically transported with hydrogen chloride. Iron can also be

transported with hydrogen bromide (1020 → 900 °C) [77]. The transport equation (88) exemplarily describes the processes.

$$Ni(s) + 2\ HCl(g) \rightleftharpoons NiCl_2(g) + H_2(g) \qquad (88)$$
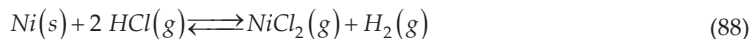
Some elements, such as molybdenum, tungsten, rhenium, gallium, germanium, tin and antimony can be transported with water via the gas phase. The transport is based on the formation of volatile oxides respectively acids. Besides the volatile acids $H_2MoO_4$ respectively $H_2WO_4$, one has also to consider gaseous oxides as transport effective species for the transport of molybdenum and tungsten in the given temperature range. Molybdenum and tungsten can be crystallized by adding iodine *and* water via exothermic chemical transport reactions (Mo: 1050 → 1150 °C, W: 800 → 1000 °C) [78, 79].

**Oxygen as transport agent**. Oxygen can function as transport agent for a series of noble metals – ruthenium, rhodium, iridium, platinum and silver [80 - 82]. In doing so, the transport always takes place at relatively high temperatures in strong endothermic reactions under the formation of volatile oxides. Thus, platinum is transported from 1500 °C to $T_1$, silver from 1400 °C to $T_1$, iridium from 1325 to 1125 °C. In particular, the chemical transport of iridium takes place at low oxygen partial pressure and high transport temperatures. Under these conditions, the formation of the solid iridium (IV) oxide can be suppressed.

$$Pt(s) + O_2(g) \rightleftharpoons PtO_2(g) \qquad (89)$$

$$Ag(s) + 1/2\ O_2(g) \rightleftharpoons AgO(g) \qquad (90)$$

$$Ir(s) + 3/2\ O_2(g) \rightleftharpoons IrO_3(g) \qquad (91)$$

### 3.2.2. Chemical vapor transport of intermetallic phases

If one refers to intermetallic phases, solids are meant which are built up by two or more metal atoms. Sometimes there is a differentiation between alloy and intermetallic compounds. In the literature, however, these terms are not used uniformly. In order to avoid misunderstanding, we solely use the term intermetallic phase. It includes metallic solids that are composed stoichiometrically as well as those with phase ranges respectively solid solutions. Solids, which are formed from metals and the semi-metals boron, silicon, germanium and antimony, can be dealt with as well due to their behavior during chemical transports.
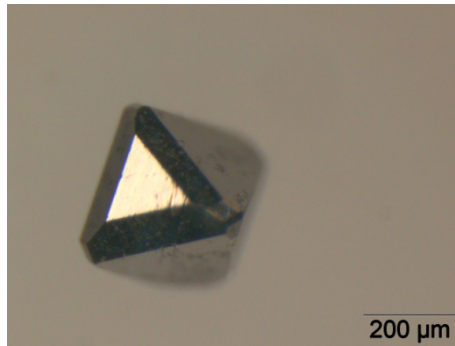
**Figure 16.** Crystal of $FeSi_{0.25}Ge_{0.75}$ grown by chemical vapor transport.

The chemical transport of intermetallic phases principally follows the one of metals. Nowadays, a variety of examples of transports of intermetallic phases is known [2, 83]. In intermetallic phases *all* components of the solid have to be transferred to the gas phase under formation of volatile gas species under the same conditions. Intermetallic phases can be obtained in particular if the elements are also obtained with the same transport agent. Examples can be found in the systems molybdenum/tungsten, cobalt/nickel, and copper/silver. Exceptions to this general rule can be found if the amount of the free enthalpy of formation of the intermetallic phase is especially high, e.g. in the systems chromium/germanium, cobalt/germanium, iron/germanium, nickel/tin or copper/tin. Chemical transport reactions are not only an alternative method for synthesis and crystal growth of intermetallic phases with high melting temperatures. They are preferable in particular for the just mentioned processes:

–One or more components of the intermetallic phase have a high vapor pressure at melting temperature.

–The intermetallic phase decomposes, e.g. peritectically before the melting temperature is reached.

–The intermetallic phase shows one or more phase changes before the melting temperature is reached.

Plenty intermetallic systems show the characteristic of the appearance of numerous solid phases with similar stabilities. Thus, often incongruent vapor transports with different composition of source and sink solid can be observed. The directed deposition of the solid with defined composition can be influenced by the composition of the source solid, the kind of the transport agents and its concentration, and the temperatures of the source and sink side as well as the resulting temperature gradient [2]. Thus, it is possible to obtain low temperature modifications of polymorphic phases in form of single-crystal. Their preparation only rarely succeeds with other methods. FeGe is an example of this in the cubic modification (575 → 535°C, [85, 86]). Likewise, the crystallization of $Fe_3Ge$ is possible by vapor transport [850…900 → 950…1000°C; [85]) despite of the peritectoid behavior of this phase, see Figure 17.
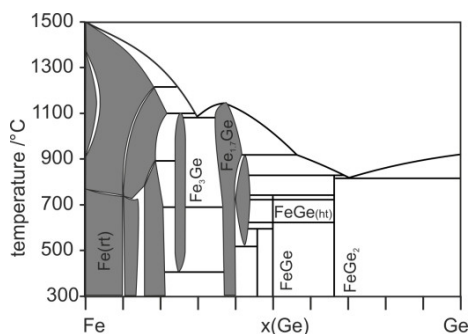
**Figure 17.** Phase diagram of the system Fe/Ge, according to [84, 85].

**Iodine as transport agent**. Due to the fact that the transport behavior of the intermetallic phases often follows that of the elements, iodine is the most commonly used transport. Apart from iodine, combinations of iodine and aluminum(III), gallium(III), or indium(III) iodide are used as transport agents as well. Other transport agents and transport-effective additives, respectively, are the halogens chlorine and bromine as well as hydrogen chloride, copper(II) chloride, manganese(II) chloride, the mercury(II) halides, tellurium(IV) chloride, and iron(II) bromide in individual cases.

As an example, the system iron-silicon can be presented. All binary phases, $Fe_2Si$, $Fe_5Si_3$, $FeSi$, and $FeSi_2$, can be crystallized by CVT reactions with iodine [87]. On the iron-rich side to $FeSi$, the exothermic transport takes places ($T_1 \rightarrow T_2$) with deposition temperatures between 700 and 1030 °C. The transport behavior parallels that of the elemental iron. If the transport efficiency of the individual gas species is considered for the reaction of $FeSi$ with iodine the transport equation (92) can be derived.

$$FeSi(s) + 7/2\, I_2(g) \xrightleftharpoons FeI_3(g) + SiI_4(g) \tag{92}$$
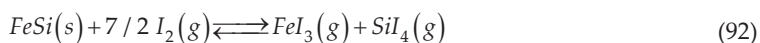
**Halogen as transport additive – halides as transport agent**. Most often, the added iodine is not the transport agent but the silicon(IV) iodide that was formed from it. Thus this transport is similar to that of silicon with $SiI_4$. The following transport equation (93) can be formulated for the *endothermic* transport of the silicon-rich phase $FeSi_2$ [87]:

$$FeSi_2(s) + 2\, SiI_4(g) \xrightleftharpoons 3\, SiI_2(g) + FeI_2(g) \tag{93}$$
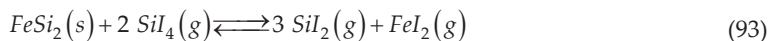
The CVT in the Cr-Si system by adding the halogens chlorine, bromine, and iodine is well examined and thermodynamically understood [89, 90]. $Cr_3Si$, $Cr_5Si_3$, $CrSi$, and $CrSi_2$ can be deposited by adding chlorine from 1100 to 900 °C. At the same temperatures, $Cr_3Si$, $Cr_5Si_3$, $CrSi$, and $CrSi_2$ can be deposited with bromine. The transport with iodine, on the other hand,

takes place exothermically from 900 to 1100 °C. In this process, Cr₃Si, Cr₅Si₃, CrSi, and CrSi₂ can be deposited. In all three cases, transport mechanisms are clearly different. If one considers the transport efficiency of the individual gas species, the following transport equations are derived:

$$Cr_5Si_3(s) + 19\ SiCl_4(g) \rightleftharpoons 5\ CrCl_2(g) +\ 22\ SiCl_3(g) \tag{94}$$

$$CrSi_2(s) + 8\ SiCl_4(g) \rightleftharpoons CrCl_2(g) + 10\ SiCl_3(g) \tag{95}$$

$$CrSi_2(s) + 3\ SiBr_4(g) \rightleftharpoons CrBr_2(g) + 5\ SiBr_2(g) \tag{96}$$
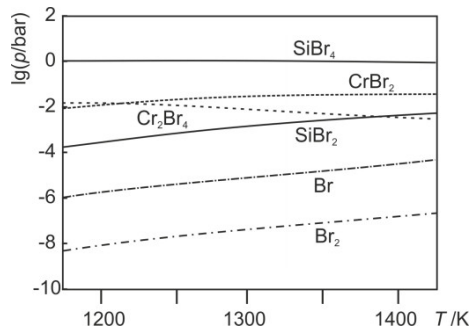
$$CrSi_2(s) + 10\ I(g) \rightleftharpoons CrI_2(g) + 2\ SiI_4(g) \tag{97}$$
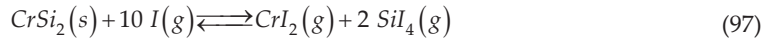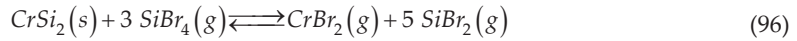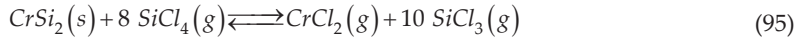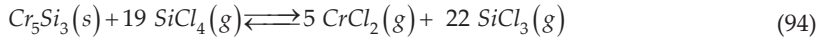
In the first three cases, the transport agent is not the added chlorine or bromine, respectively, but the silicon(IV) chloride or bromide, respectively, which was formed in a simultaneous reaction, Figure 18. In contrast to this, iodine functions directly as the transport agent when added.



**Figure 18.** Composition of the gas phase for the transport of CrSi using bromine, according to [89].

**Intermetallic phases with wide phase range**. Intermetallic systems often show the formation of solid solutions or at least vast regions of solubility of the components. For these characteristic phase relations, the crystallization of phases with defined composition is demanding. As a special example, molybdenum and tungsten are two metals with very high melting points. They are isotypic and completely mixable in the solid and liquid state. Here the formation of specified compositions of mixed crystals molybdenum-tungsten from the melt requires great experimental effort due to the exsolution within the solidus-liquidus-region. With the help of

CVT reactions, this succeeds far below the liquidus curve. As both metals can be transported with the same transport agent under the same conditions, molybdenum-tungsten mixed-crystals can be deposited by CVT from 1000 to 900 °C when mercury(II) bromide is added [91]. The transport equation (98) describes the process:

$$Mo_{1-x}W_x(s) + 2\,HgBr_2(g) \rightleftharpoons (1-x)\,MoBr_4(g) + xWBr_4(g) + 2\,Hg(g) \qquad (98)$$
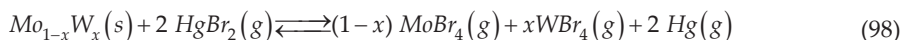
In the following binary systems, mixed-crystals are transportable in an analogous way: cobalt-nickel [91, 92], iron-nickel, silver-copper, gold-copper, copper-nickel, gold-nickel [93], and copper-gallium [94].

### 3.2.3. Chemical vapor transport of halides

The majority of metal halides are sufficiently stable to evaporate undecomposed. Thus, most of them can be volatilized by distillation or sublimation; the deposition occurs at lower temperatures. Some metal halides decompose at higher temperatures either to the elements or to a metal-rich halide and the according halogen. In this manner platinum(II) chloride decomposes notably above 500 °C forming solid platinum and gaseous chlorine. Otherwise, copper(II) chloride decomposes above 300 °C under the formation of copper(I) chloride and chlorine. The tendency of decomposing generally increases from the fluorides to the iodides. Some metal halides disproportionate while heating: molybdenum(III) chloride essentially dissociates above 600 °C under the formation of solid molybdenum(II) chloride and gaseous molybdenum(IV) chloride.
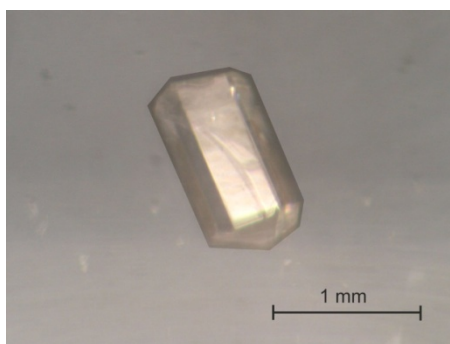


**Figure 19.** Crystal of CeCl$_3$ grown by chemical vapor transport

Beside the sublimation processes, metal halides can be obtained by CVT reactions, too. Four different types of solid-gas reactions are of relevance. Additionally, further reactions of different kinds are known, which can be used for the transport of metal halides. However, their application is limited so far. An overview on the CVT of halides is provided by Opper-mann [95]; for more current references of CVT of the halides see [2].

**Formation of halogen-rich halides**. If halides of a concerned metal exist in different oxidation states, decreasing boiling temperatures for increasing oxidation numbers (halogen-rich halides) can be observed. This behavior is effected by the covalence of the metal-halogen-compound, which increases with higher oxidation number. Thus the formation of higher volatile halide species is possible by reaction of a metal-rich halide with a halogen. This kind of transport reaction is often observed with halides of the transition metals (99).

$$CrCl_3(s) + 1/2\, Cl_2(g) \rightleftharpoons CrCl_4(g) \tag{99}$$
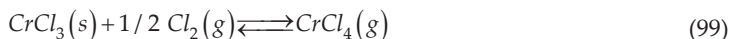
However, the tendency of decomposition of halides with higher oxidation numbers increases at the same time. For this reason, the vapor transport by halogenation is restricted in temperature. Or, in another way, a high partial pressure of the halogen is needed to form a sufficiently high pressure of the transport effective metal halide species. Gaseous ruthenium(IV) bromide is formed during the transport of ruthenium(III) bromide with bromine (100); [96]. However, a high bromine pressure of 15 bar is required to cause a sufficient transport effect.

$$RuBr_3(s) + 1/2\, Br_2(g) \rightleftharpoons RuBr_4(g) \tag{100}$$
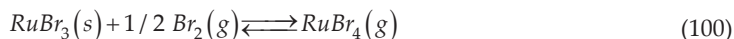
Generally, the halogen is used as a transport agent, which is also contained in the solid. Sometimes, however, another halogen is used as the transport agent (101), [97]. Here, during the crystallization a small amount of transport agent bromine condenses and a solid of the composition $VCl_{2.97}Br_{0.03}$ forms in the sink.

$$VCl_3(s) + 1/2\, Br_2(g) \rightleftharpoons VCl_3Br(g) \tag{101}$$
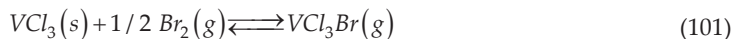
**Conproportionation reactions**. Transition metals can appear in different binary halides, which are similarly stable under vapor transport conditions. This particularly applies for metals of group 5 and 6. This behavior can be used in order to transport a solid metal halide in which the metal has a low oxidation number with a gaseous metal halide in which the metal has an oxidation number that is higher by two units or more. The transport of niobium(III) chloride with niobium(V) chloride as transport agent is given as an example [1]. Gaseous niobium(IV) chloride is formed, which disproportionates in the sink of transport to form solid niobium(III) chloride and gaseous niobium(V) chloride. Frequently, the according halogen is used as transport additive instead of the transport agent that was formulated in the transport equation. Thereby, the actual effective transport agent forms in a preliminary reaction of the transport additive with the solid. Additional examinations and/or thermodynamic model calculations are necessary in order to decide whether the added halogen or a higher halide that is formed by the halogen is the actual transport agent.

$$NbCl_3(s) + NbCl_5(g) \rightleftharpoons 2\,NbCl_4(g) \tag{102}$$
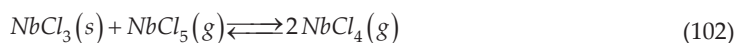
**Formation of gas complexes**. The term *gas complex* refers to a gaseous metal-halogen compound in which several metal atoms are bonded with each other by halogen bridges. Gas complexes with several identical metal atoms, such as $Al_2Cl_6$, are also called *homeo complexes*. Those with different metal atoms, such as $NaAlCl_4$, are labeled *hetero complexes* [98 - 100]. The CVT of metal halides under formation of gas complexes is realized for solid metal halides with a high boiling temperature under addition of a high volatile halide, particularly often an aluminum halide. The aluminum halides have low boiling temperatures and form stable gas complexes with a variety of metal halides. Gallium(III) halides, indium(III) halides, and iron(III) halides are used as transport agents as well.

*Metal monohalides*, like the alkali metal halides $MX$ form gas complexes of the composition $MAlX_4$ by adding the aluminum halides $AlX_3$. These complexes are characterized by an extremely high stability. However, the solid and liquid ternary halides of these compositions are to stable to reverse the transport equilibrium under crystallization of the alkali metal halides. That is because in the sink not the alkali metal halides but a different ternary phase is always deposited. Accordingly, this also applies when gallium(III) halides, indium(III) halides, and iron(III) halides are used as transport agents.

*Metal dihalides* $MX_2$ form gas complexes of the composition $MAl_2X_8$ and $MAlX_5$ when the trihalides of aluminum, gallium, and iron are used as a transport agent. As an example, the transport of manganese(II) chloride with aluminum-chloride, gallium-chloride, and indium-chloride is discussed in detail [102]. Additionally, the formation of larger gas complexes of the composition $MAl_3Cl_{11}$ and $MAl_4Cl_{14}$ has been reported [101, 102]. At moderate temperatures of about 400 °C the dimer $Al_2Cl_6$ acts as a transport agent and the transport of metal dihalides takes place via $MnAl_2Cl_8$ as transport-effective species (103).

$$MnCl_2(s) + Al_2Cl_6(g) \rightleftharpoons MnAl_2Cl_8(g) \tag{103}$$
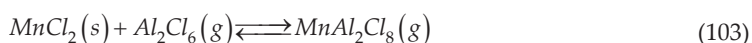
The enthalpy of formation of the complex does not entirely compensate the sublimation enthalpy of metal halide so that the transport reaction (103) is always endothermic. Under different transport conditions (> 500 °C) the transport direction can change in presence of the transport agent aluminum(III) chloride as monomeric $AlCl_3(g)$. Additionally, the formation of complexes of the composition $MnAlCl_5$ becomes more important. This transport takes place to the hotter zone in an exothermic reaction (104).

$$MnCl_2(s) + AlCl_3(g) \rightleftharpoons MnAlCl_5(g) \tag{104}$$
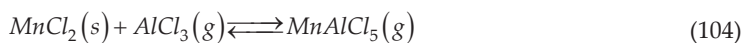
*Metal trihalides* $MX_3$ can form gas complexes of the composition $MM'_2X_9$, $MM'_3X_{12}$, and $MM'_4X_{15}$ by adding the trihalides $M'X_3$ of aluminum, gallium, and iron [32, 103, 104]. By the formation of these gas complexes even the transport of non- volatile trihalides is possible in endothermic

reactions at 500 to 400 °C [105, 106]. This way, chromium(III) chloride [105] and the trihalides of the lanthanoid metals [107] can be obtained in crystalline form with aluminum(III) chloride as transport agent.

$$LnCl_3(s) + 2M'Cl_3(g) \rightleftharpoons LnM'_2X_9(g) \tag{105}$$

$$LnCl_3(s) + 2M'Cl_3(g) \rightleftharpoons LnM'_3X_{12}(g) \tag{106}$$

$$LnCl_3(s) + 2M'Cl_3(g) \rightleftharpoons LnM'_4X_{15}(g) \tag{107}$$
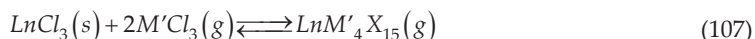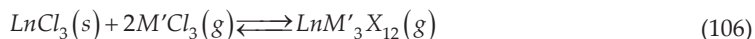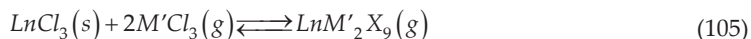
The formation of gas complexes plays an important role for the separation of the halides of the lanthanoids. In a gas stream of aluminum(III) chloride the individual lanthanoid halides form gas complexes of different stability. These complexes decompose under the formation of the halides $LnX_3$ at different places. This way, the halides of the lanthanoids can be separated in a "fractionalized chemical vapor transport" [109-118]. During this process the solid oxides can be used (108).
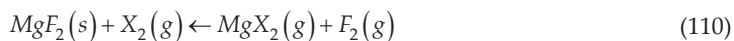
$$Ln_2O_3(s) + 3\ C(s) + 3\ Cl_2(g) \rightleftharpoons 2LnCl_3(s) + 3\ CO(g) \tag{108}$$
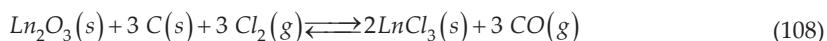
*Metal tetrahalides* UCl$_4$ and ThCl$_4$ realize a vapor transport under addition of aluminum(III) chloride [106] probably by endothermic formation of UAl$_2$Cl$_{10}$ and, respectively, ThAl$_2$Cl$_{10}$.

*Metal pentahalides* are not very common. Their vapor pressure is relatively high so that they can be sublimed without any problems and are of minor interest for transport reactions.

**Halogen transfer reactions and formation of interhalogen compounds**. In contrast to the semi- and non-metals, the fluorides of the metals have essentially higher boiling temperatures compared to the chlorides, bromides, and iodides: The boiling temperatures of aluminum fluoride is 1275 °C, those of the other halides 181 °C (AlCl$_3$), 254 °C (AlBr$_3$), and 374 °C (AlI$_3$). Thus, the variety of metal fluorides cannot be crystallized by sublimation. In a few cases, transport with silicon(IV) chloride succeeded [119, 120]. The transport reaction works due to the fact that silicon(IV) fluoride as well as silicon(IV) chloride are highly volatile compounds.

$$4\ AlF_3(s) + 3\ SiCl_4(g) \rightleftharpoons 4\ AlCl_3(g) + 3\ SiF_4(g) \tag{109}$$
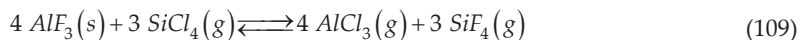
Principally, the CVT of fluorides with halogens as a transport agent is not possible via equilibria, such as (110), due to their unfavorable position. The release of fluorine, which occurs during the reaction, is thermodynamically unfavorable. Nevertheless, magnesium fluoride can be crystallized with iodine as transport agent [121]. Thermodynamic model calculations with data for the gaseous iodine fluorides IF$_n$ ($n$ = 1, 3, 5, 7) reflect the observed transport effect. These calculations suggest a significant participation of IF$_5$ in the transport process according to (111).

$$MgF_2(s) + X_2(g) \leftarrow MgX_2(g) + F_2(g) \tag{110}$$

(X = Cl, Br, I)

$$5MgF_2(s) + 6\,I_2(g) \rightleftharpoons 5\,MgI_2(g) + 2\,IF_5(g) \tag{111}$$
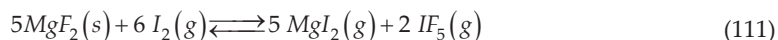
### 3.2.4. Chemical vapor transport of oxides

Oxides represents the most reported substance group with more than 600 examples of chemical vapor transports. For more details and particularized references of CVT of the oxides see [2]. Simple binary oxides, such as zinc(II) oxide and iron(III) oxide, have been crystallized as well as oxides with complex anions, such as phosphates or sulfates, and oxides with several cations, such as $ZnFe_2O_4$ or $Co_{1-x}Ni_xO$. Metal oxides are thermodynamically very stable compounds. However, only a few of them evaporate undecomposed; among them are $CrO_3$, $MoO_3$, $WO_3$, $Re_2O_7$, GeO, SnO, PbO, and $TeO_2$. Most of the metal oxides decompose by evaporation of oxygen. Besides, the respective metal or a metal-rich oxide is formed. The latter can be present as condensed phase or as a gas. The following three examples show the different thermal behavior of metal oxides:

$$2\,ZnO(s) \rightleftharpoons 2\,Zn(g) + O_2(g) \tag{112}$$

$$2\,SiO_2(s) \rightleftharpoons 2\,SiO(g) + O_2(g) \tag{113}$$

$$6\,Fe_2O_3(s) \rightleftharpoons 4\,Fe_3O_4(s) + O_2(g) \tag{114}$$
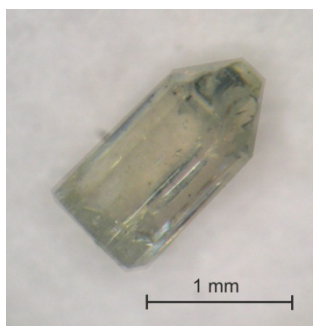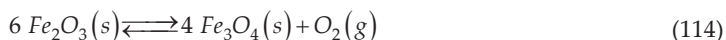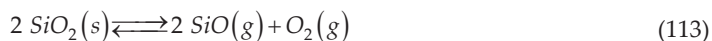


**Figure 20.** Crystal of ZnO grown by chemical vapor transport.

The thereby released oxygen partial pressure is called the **decomposition pressure**. It is the leading determinant of the transport behavior and the composition of the crystallized oxide. The transport of $Fe_2O_3$ can be served as an example: If the oxygen partial pressure in the system is higher than the decomposition pressure of $Fe_2O_3$, this compound is stable as a solid; if it is lower, the reduced solid, $Fe_3O_4$ will be formed. If the oxygen partial pressure is identical with the decomposition pressure at a certain temperature, both soli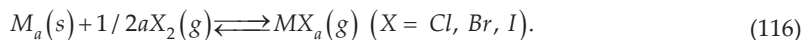d phases will co-exist. If the logarithm of a co-existence decomposition pressure is plotted against the reciprocal temperature for different oxides of a metal, the **phase barogram** of the system will be obtained. By means of the phase relations presented in the phase barograms, the choice of suitable parameters for phase pure transports respecting the temperature and the temperature gradient becomes possible [2].

A variety of transport agents has been investigated for oxides, but chlorinating equilibria proved most suitable. Apart from chlorine and hydrogen chloride, tellurium(IV) chloride is an important transport agent. Tellurium(IV) chloride is used especially when the oxygen partial pressure in the system varies, and the setting of the oxygen partial pressure is of essential importance for the transport behavior. Some other chlorinating additives include phosphorus(V) chloride, niobium(V) chloride, selenium(IV) chloride, and tetrachloromethane as well as mixtures of sulfur/chlorine, vanadium(III) chloride/chlorine, and chromium(III) chloride/chlorine. Due to unfavorable equilibrium positions, brominating and iodinating equilibria are of minor importance for the CVT of oxides. Here, transport agents or transport effective additives, respectively, are: bromine and iodine, hydrogen bromide and hydrogen iodide, phosphorus(V) bromide, niobium(V) bromide and -iodide as well as sulfur+iodine. Iodine as a transport agent and iodinating equilibria are of interest if chlorine is too oxidizing or if, as is the case with rare-earth metal oxides, stable solid oxide chlorides form. Some further transport agents or transport effective additives, respectively, are hydrogen, oxygen, water, carbon monoxide and in special cases, fluorine or hydrogen fluoride. In some cases, the solid oxides can form gaseous oxide halides: transport-effective species, which contain both oxygen and halogen atoms.

**Halogens as transport agents**. The process of dissolution of an oxide in the gas phase by heterogeneous reaction with a halogen can be split into two partial reactions of decomposition of the oxide and the halogenation of the metal:

$$M_aO_{1/2a}(s) \Longleftrightarrow M_a(s) + 1/4aO_2(g) \tag{115}$$
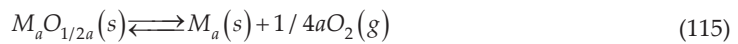
($a$ = oxidation number of the metal)
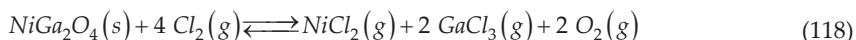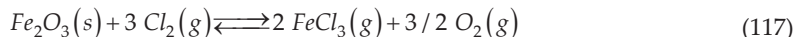
$$M_a(s) + 1/2aX_2(g) \Longleftrightarrow MX_a(g) \ (X = Cl, Br, I). \tag{116}$$

Due to the higher stability of the chloride gas species compared to the bromide and the resulting equilibrium position, mostly chlorine is used as the transport agent for the CVT of

oxides. In the process, sufficiently stable gas species are formed with adequately high partial pressures ($p > 10^{-5}$ bar) and sufficiently high partial pressure differences along the temperature gradient. The transports of $Fe_2O_3$ and $NiGa_2O_4$ with chlorine shall be used as examples.

$$Fe_2O_3(s) + 3\ Cl_2(g) \rightleftharpoons 2\ FeCl_3(g) + 3/2\ O_2(g) \tag{117}$$

$$NiGa_2O_4(s) + 4\ Cl_2(g) \rightleftharpoons NiCl_2(g) + 2\ GaCl_3(g) + 2\ O_2(g) \tag{118}$$

Halogens are also suited as transport agents for oxides when gaseous oxide halides are formed. This way, for example, the transport of molybdenum(VI) oxide with chlorine succeeds:

$$MoO_3(s) + Cl_2(g) \rightleftharpoons MoO_2Cl_2(g) + 1/2\ O_2(g) \tag{119}$$
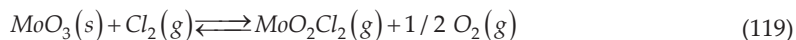
Instead of introducing pure halogens, decomposition of less stable halides, such as $PtX_2$ ($X$ = Cl, Br, I), can be used to form halogens. If mercury halides are employed as transport agents, the equilibrium position of the transport reaction will shift compared to elemental halogen. By decomposing gaseous mercury halides to the elements (120), additional gas species are formed. There will be a change of the entropy balance shifting the equilibrium position to the side of the reaction products.

$$HgX_2(g) \rightleftharpoons Hg(g) + X_2(g) \tag{120}$$

**Transport with addition of hydrogen halides**. Hydrogen chloride, and less frequently hydrogen bromide and hydrogen iodide, are often used and are effective transport agents for the CVT of oxides. In special cases, as for silicates, also hydrogen fluoride is used as a transport agent. During the transport of a binary oxide with a hydrogen halide, a gaseous metal halide is formed besides water (121). The transport of zinc oxide with hydrogen chloride is an example:

$$ZnO(s) + 2\ HCl(g) \rightleftharpoons ZnCl_2(g) + H_2O(g) \tag{121}$$
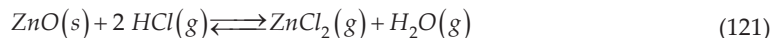
The simple transport equation by forming the respective chloride and water only applies if no volatile acids, such as $H_2MoO_4(g)$, hydroxides, and oxide halides, respectively, are formed. Using hydrogen halides, often a more favorable equilibrium position can be achieved instead of halogens. As a feasible hydrogen halide source, the ammonium halides ($NH_4X$, $X$ = Cl, Br, I) can be used. These solids are easy to handle and to dose. They decompose to ammonia and hydrogen halide at increased temperature. However, the formation of ammonia creates a

reducing atmosphere. This can lead to a reduction of the gas species and/or the solid phase. In some cases, in which the transport of oxides with moisture-sensitive halides, such as aluminum(III) chloride or tellurium(IV) chloride, is described, hydrogen chloride can be expected as the transport agent. Traces of water, which can never be excluded completely, cause the formation of hydrogen halide.

**Tellurium(IV) halides as transport agents**. Tellurium(IV) chloride is a flexible transport agent, which can especially be used for oxides of the transition metals and compounds with complex anions [31, 122]. The simplified transport equation (122) can be assumed:

$$ZrO_2(s) + TeCl_4(g) \rightleftharpoons ZrCl_4(g) + TeO_2(g) \tag{122}$$
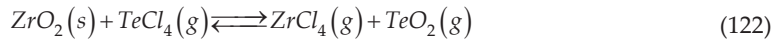
In this simplification, however, the equilibria (123) to (128) in the system Te/O/Cl are not considered. Reichelt discussed the complex reaction behavior of tellurium(IV) chloride in detail [123].

$$TeCl_4(g) \rightleftharpoons TeCl_2(g) + Cl_2(g) \tag{123}$$

$$TeCl_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons TeOCl_2(g) \tag{124}$$

$$TeOCl_2(g) \rightleftharpoons TeO(g) + Cl_2(g) \tag{125}$$

$$TeO_2(g) \rightleftharpoons 1/2 \, Te_2(g) + O_2(g) \tag{126}$$

$$Te_2(g) \rightleftharpoons 2 \, Te(g) \tag{127}$$

$$Cl_2(g) \rightleftharpoons 2 \, Cl(g) \tag{128}$$
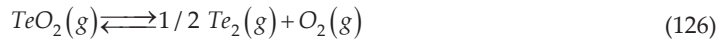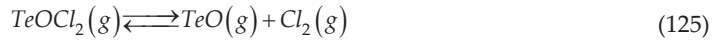
Creating such a complex red-ox system, tellurium(IV) chloride is specially suited as a transport additive for oxide systems with a wide range of oxygen partial pressures between $10^{-25}$ and 1 bar. Thereby, at low oxygen partial pressures, the reduced gas species $TeCl_2$, $Te_2$, Te, $Cl_2$, and Cl dominate. The transport of $Mn_3O_4$ with tellurium(IV) chloride can be served as an example: The gas phase consists of the dominating gas species $MnCl_2$, $Te_2$, $Mn_2Cl_4$, Te, TeO, and $TeCl_2$ (with $p(i) > 10^{-4}$ bar in the temperature range of about 1000 °C; see Figures 3.4). The partial pressures of the other oxygen-containing gas species $TeO_2$ and $TeOCl_2$ are clearly below $10^{-5}$ bar [124]. At higher oxygen partial pressures, the amount of higher oxidized gas species

$TeO_2$ and $TeOCl_2$ becomes significantly higher, for example during the transport of manganese(III) oxide. Here, at1000 °C, the gas phase contains the species $O_2$, $Cl_2$, $TeOCl_2$, $TeO_2$, $MnCl_2$, $Cl$, $TeCl_2$, and $TeO$ in the pressure range between 1 and $10^{-5}$ bar [124].
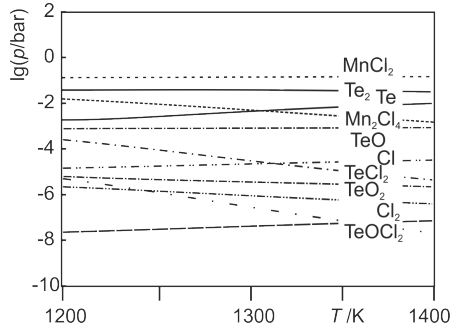


**Figure 21.** Composition of the gas phase for the transport of $Mn_3O_4$ using $TeCl_4$, according to [124].

In particular, tellurium(IV) chloride proves an ideal transport additive for those oxides that differ only slightly in their composition and stability and thus are thermodynamically stable only in narrow ranges of the oxygen partial pressure. Thus, the chemical vapor transport of the *Magnéli*phases of vanadium, $V_nO_{2n-1}$ ($n = 2 \dots 8$), succeeded with tellurium(IV) chloride [123, 125, 126]; see Figure 22. Tellurium(IV) chloride is also suitable for the transport of oxide phases that show homogeneity ranges that are dependent on the oxygen partial pressure, such as "$VO_2$" [31, 127] and for oxides of transition metals that have similar stabilities, such as MnO and $Mn_3O_4$ [123, 128]. Similar redox systems form when tellurium(IV) bromide ($TeBr_4$) [129] and $TeI_4$ [130] are used as transport agents.
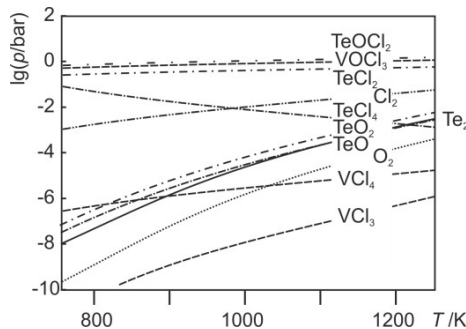


**Figure 22.** Composition of the gas phase for the transport of $VO_2$ using $TeCl_4$, according to [2, 125].

**Reactions with combined transport additives**. The combination of two transport additives is often used, for example the combination of sulfur, selenium or carbon in addition to the halogens. These gas mixtures form complex redox systems and can be treated in a similar way

to tellurium(IV) chloride. The mechanism of the combination of sulfur+iodine is described exemplarily by equation (129). Here, sulfur transfers oxygen; iodine transfers gallium. The transport agent combinations carbon+chlorine and carbon+bromine are introduced in the form of $CCl_4$ (130) and $CBr_4$, respectively. The formation of gaseous $SO_2$ and CO, respectively, causes a more balanced equilibrium position compared to the reactions in which oxygen is formed. Due to the stability of the formed oxide gas species the reaction equilibrium position is shifted to the side of the gaseous reaction products.

$$2\ Ga_2O_3(s) + 3/2\ S_2(g) + 6\ I_2(g) \rightleftharpoons 4\ GaI_3(g) + 3\ SO_2(g) \qquad (129)$$

$$Y_2O_3(s) + 3\ CCl_4(g) \rightleftharpoons 2\ YCl_3(g) + 3\ CO(g) + 3\ Cl_2(g) \qquad (130)$$

In some cases, a transport agent combination consisting of a halide and a halogen is applied, for example for the transport of $SiO_2$ with $CrCl_4+Cl_2$. In this process, the surplus of halogen leads to formation of more volatile oxidized gas species ($CrO_2Cl_2$).

$$SiO_2(s) + CrCl_4(g) + Cl_2(g) \rightleftharpoons SiCl_4(g) + CrO_2Cl_2(g) \qquad (131)$$
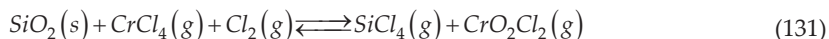
The usage of phosphorus(III) halides, $PCl_3$ and $PBr_3$, in addition to the respective halogens causes the formation of the pentahalides. The phosphorus(V) halides proved to be suitable transport agents as well as the analogues $NbCl_5$ and $TaCl_5$, as they have both a halogenating effect on the metal and a transport effective for oxygen (132, 133).

$$LaPO_4(s) + 3\ PCl_3(g) + 3\ Cl_2(g) \rightleftharpoons LaCl_3(g) + 4\ POCl_3(g) \qquad (132)$$

$$Nb_2O_5(s) + 3\ NbCl_5(g) \rightleftharpoons 5\ NbOCl_3(g) \qquad (133)$$

Aluminum(III) chloride is not suited for the transport of oxides because aluminum oxide is formed. Observed transport effects can most often be traced back the formation of hydrogen chloride.

### 3.2.5. Chemical vapor transport of oxides with complex anions

The chemical vapor transport of oxides with complex anions represents few examples of crystallization of

- sulfates, selenates, and tellurates
- phosphates, arsenates, and antimonates

- silicates

- borates
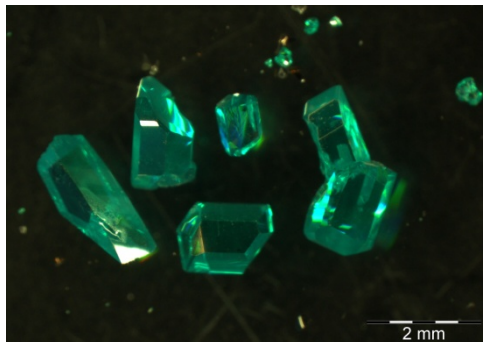


**Figure 23.** Crystals of CuTe$_2$O$_5$ grown by chemical vapor transport.

These complex oxides differ from other multinary oxides ("double oxides") by their high heats of reaction for the formation from binary oxides. In terms of their chemical structure, they are different by the low co-ordination number of the non-metal. For more details and references of CVT of compounds with complex anion see [2].

The crystallization of anhydrous *sulfates* is quite challenging. Most of the representatives of this compound class show a comparatively low thermal stability (decomposition to SO$_3$ and SO$_2$+O$_2$), only the sulfates of the alkali metals melt and sublime without decomposing. For CVT, chlorine or hydrogen chloride can be used as transport agents for sulfates [2]. The transport of ZnSO$_4$ (134) can be served as an example [131, 132]. In some cases, the vapor transport could be observed when I$_2$, NH$_4$Cl, HgCl$_2$, PbCl$_2$ (135), PbBr$_2$, or SOCl$_2$ were added.

$$ZnSO_4(s) + Cl_2(g) \rightleftharpoons ZnCl_2(g) + SO_3(g) + 1/2\ O_2(g) \tag{134}$$
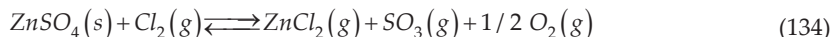
An oxidizing equilibrium gas phase is the requirement for the use of PbCl$_2$ as transport additive for some anhydrous sulfates, such as NiSO$_4$ or CuSO$_4$ [133]. In the process, chlorine is released in a pre-reaction (135); the formed chlorine functions as the actual transport agent for NiSO$_4$ (136).

$$2\ NiSO_4(s) + PbCl_2(l) \rightleftharpoons PbSO_4(s) + 2\ NiO(s) + SO_2(g) + Cl_2(g) \tag{135}$$

$$NiSO_4(s) + Cl_2(g) \rightleftharpoons NiCl_2(g) + SO_3(g) + 1/2\ O_2(g) \tag{136}$$
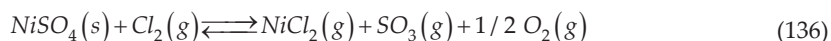
While the volatilization of aluminum (III) oxide with chlorine (as with other transport agents) in a temperature gradient is impossible due to the unfavorable equilibrium position of reaction, the crystallization of aluminum sulfate by CVT is successful using $SOCl_2$ as a transport agent [134]. The resulting transport reaction avoids the formation of free oxygen. Thus a favorable position of the heterogeneous transport equilibrium (137) is caused. The crystallization of $Cr_2(SO_4)_3$, $Ga_2(SO_4)_3$, and $In_2(SO_4)_3$ can be realized in the same way.

$$Al_2(SO_4)_3(s) + 3\ SOCl_2(g) \rightleftharpoons 2\ AlCl_3(g) + 3\ SO_2(g) + 3\ SO_3(g) \tag{137}$$
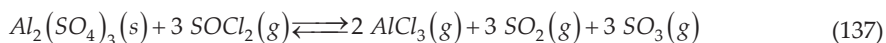
The CVT of phosphates is a preparative method for crystallization of even thermally delicate phosphates, like $Re_2O_3(PO_4)_2$ [135] and $CuP_4O_{11}$ [136]. Phosphates of transition metals with oxidation states that are not easily accessible in another ways (low numbers) can be synthesized in sealed silica ampoules and crystallized in "one-pot reactions" by CVT (e. g., $TiPO_4$, $V_2O(PO_4)$, $Cr_3(PO_4)_2$, and $Cr_2P_2O_7$). Apart from the elemental halogens $Cl_2$, $Br_2$, and $I_2$, halogen compounds ($NH_4X$ and $HgX_2$; $X$ = Cl, Br, I) as well as mixtures $P+X_2$ ($X$ = Cl, Br, I) are used. In some cases, such as $Fe_3O_3PO_4$ or $UP_2O_7$ chlorinating compounds, such as $VCl_4$, $ZrCl_4$, $HfCl_4$, and $NbCl_5$ are suitable transport agents [137]. The best results, as far as transport rates and crystal growth of anhydrous phosphates are concerned, were achieved with chlorine or mixtures of phosphorus+iodine as transport agents [138].

$$Co_2P_2O_7(s) + 2\ Cl_2(g) \rightleftharpoons 2\ CoCl_2(g) + 12\ P_4O_{10}(g) + O_2(g) \tag{138}$$

$$Ni_2P_4O_{12}(s)\ + 2/3\ P_4(g) + 4/3\ PI_3(g) \rightleftharpoons 2\ NiI_2(g) + 2\ P_4O_6(g) \tag{139}$$
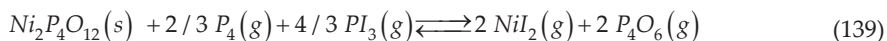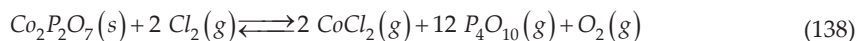
The transport of anhydrous phosphates with iodine and reducing additives does not take place via $P_4O_{10}$. Observations during the transport of $Cr_2P_2O_7$ [138] with iodine in the presence of a surplus of CrP are as remarkable in this context as the transport of $WOPO_4$ and $WP_2O_7$ adjacent to WP [139]. In all three cases, a *simultaneous transport* of phosphides and phosphates due to an endothermic reaction is found experimentally. Experiments with the transport balance show that phosphide and phosphate migrate from the source to the sink in a single stationary state if the two condensed phases are provided in a certain ratio with respect to their amounts of substance. This behavior indicates a *coupled vapor transport reaction* of the two phases.

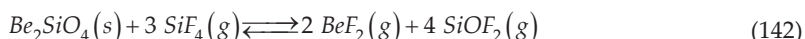$$Cr_2P_2O_7(s)\ + 8/3\ CrP(s)\ + 14/3\ I_2(g) \rightleftharpoons 14/3\ CrI_2(g)\ + 7/6\ P_4O_6(g) \tag{140}$$
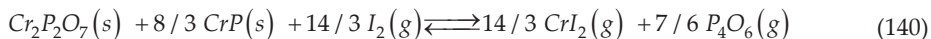
In contrast to anhydrous phosphates, metal *arsenates(V), antimonates(V), and vanadates(V)* show a clearly lower thermal stability. The compounds tend, more easily than phosphates, toward the formation of oxygen and gaseous $As_4O_6$, $Sb_4O_6$, and $VO_2$, respectively. The limited stability
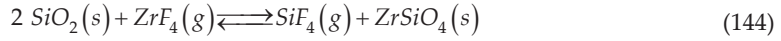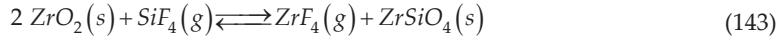
**Figure 24.** Crystals of PrPO$_4$ grown by chemical vapor transport.

of arsenates and antimonates, combined with the volatility of As$_4$O$_6$ and Sb$_4$O$_6$, seems to be favorable for CVT of these compounds. Hence, Weil [140] describes the successful CVT experiments aiming at the crystallization of different anhydrous arsenates with chlorine, a mixture of HCl +H$_2$ (addition of NH$_4$Cl), and HgCl$_2$ as the transport agent. For more details and references of CVT of the phosphates, arsenates, antimonates, and vanadates see [2].

While there are no indications on chemical vapor transport of *carbonates*, a number of reports on the CVT of *silicates* are given. Early on, the assumption was made that transport reactions with participation of the gas phase are involved in mineral-forming processes of silicates in nature [141]. Indeed, only the migration of europium(II) silicates (Eu$_2$SiO$_4$, EuSi$_2$O$_5$) at high temperatures with HCl as transport agent (141) and the crystallization of Be$_2$SiO$_4$ with SiF$_4$ (142) are based on transport reactions of the minerals [142].

$$Eu_2SiO_4(s) + 6\ HCl(g) \rightleftharpoons 2\ EuCl_2(g) + SiCl_2(g) + 3\ H_2O(g) + 1/2\ O_2(g) \qquad (141)$$

$$Be_2SiO_4(s) + 3\ SiF_4(g) \rightleftharpoons 2\ BeF_2(g) + 4\ SiOF_2(g) \qquad (142)$$

In contrast to reversible CVT reactions in the direct sense, the crystallization of silicates with participation of the gas phase can be traced back to partial transport reactions. The formation of *zircon* ZrSiO$_4$ from zirconium dioxide in silica ampoules when silicon(IV) fluoride is added, has been discussed by Schäfer [1]. The reactions (143) (over the solid ZrO$_2$/ZrSiO$_4$) and (144) (over the solid SiO$_2$/ZrSiO$_4$) describe the process completely. The partial equilibria allow sufficiently high pressures for SiF$_4$ and ZrF$_4$, so that the interdependent transport of silicon and zirconium becomes possible. Here, the migration takes place via the fluorides under isothermal (!) conditions in the gradient of the respective chemical potentials. The formation of other silicates, like *topaz* (Al$_2$SiO$_4$F$_2$) from AlF$_3$ and SiO$_2$ [143] takes place in a similar way.

$$2\ ZrO_2(s) + SiF_4(g) \rightleftharpoons ZrF_4(g) + ZrSiO_4(s) \tag{143}$$

$$2\ SiO_2(s) + ZrF_4(g) \rightleftharpoons SiF_4(g) + ZrSiO_4(s) \tag{144}$$

Boron(III) oxide forms numerous ternary and multinary oxido compounds. Nevertheless, there are hardly any indications on the chemical vapor transport of **borates**. Only the migration of $CrBO_3$, $FeBO_3$, $BPO_4$, and $Cr_2BP_3O_{12}$ in the temperature gradient is detected for sure [2, 144].

$$FeBO_3(s) + 3\ HCl(g) \rightleftharpoons FeCl_3(g) + HBO_2(g) + H_2O(g) \tag{145}$$

Several other borates were obtained as a by-product during the synthesis of *boracites* $M_3B_7O_{13}X$ ($M$ = metal atom with the oxidation number II, $X$ = Cl, Br, I). Boracites can be crystallized well with the help of CVT reactions, in contrast to the halogen-free borates. [145]. Boracites are transported with water and the corresponding hydrogen halide. The constituent compounds $MO$, $MX_2$, and $B_2O_3$ are separately put in a *two-crucible technique* apparatus [146] or a *three-crucible technique* apparatus [145, 147, 148]. The transport takes place isothermally at about 900 °C along an *activity gradient* of the components. The metal dihalildes $MX_2$ as well as $BX_3$, $B_3O_3X_3$, and $HBO_2$ are considered as active transport species [149].

$$MX_2(s) \rightleftharpoons MX_2(g) \tag{146}$$

$$MO(s) + 2\ HX(g) \rightleftharpoons MX_2(g) + H_2O(g) \tag{147}$$

$$B_2O_3(s) + 6\ HX(g) \rightleftharpoons 2\ BX_3(g) + 3\ H_2O(g) \tag{148}$$

$$3\ B_2O_3(s) + 6\ HX(g) \rightleftharpoons 2\ (BOX)_3(g) + 3\ H_2O(g) \tag{149}$$

$$B_2O_3(s) + H_2O(g) \rightleftharpoons 2\ HBO_2(g) \tag{150}$$
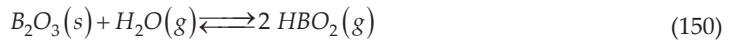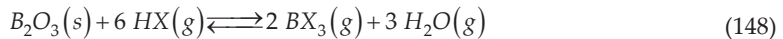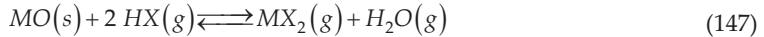
### 3.2.6. Chemical vapor transport of chalcogenides

Chemical vapor transports of metal sulfides, selenides, and tellurides have been examined in detail. The first investigations were made in the 1960s by Nitsche [150]. To date, the number of examples that are known from the literature [2] is only exceeded by those of the oxides.

Nonetheless, the CVT of chalcogenide compounds clearly differs from that of the oxides. Due to the lower thermodynamic stability of the metal sulfides, selenides, and tellurides compared to the oxides most often iodine or iodine compounds are used as transport agents. Thus more balanced equilibria of the transport reactions of sulfides, selenides, and tellurides can be achieved, in contrast to the one of the respective oxide (151).

$$ZnQ(s) + X_2(g) \rightleftharpoons ZnX_2(g) + 1/2 Q_2(g), \; \left( X = \; Cl, \; Br, \; I; Q = \; O, \; S, \; Se, \; Te \right) \qquad (151)$$
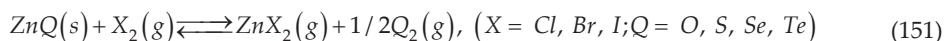
| $\Delta_r G^0{}_{1000}/kJ \cdot mol^{-1}$ | Cl, | Br, | I |
|---|---|---|---|
| ZnO | −26 | +22 | +103 |
| **ZnS** | −104 | −56 | **+25** |
| **ZnSe** | −123 | −57 | **+7** |
| **ZnTe** | −170 | −122 | **−41** |
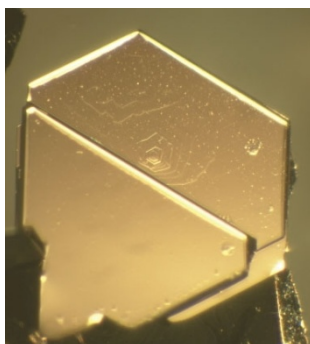


**Figure 25.** Crystal of TaS$_2$ grown by chemical vapor transport.

**Transport of Sulfides**. A large number of examples of binary and ternary sulfides as well as quaternary and even multinary sulfides, such as FeSn$_4$Pb$_3$Sb$_2$S$_{14}$ [151] are available by CVT reactions [2]. This is indeed noteworthy, because in these cases the transport agent is appa‐ rently able to transfer *all* cations that are present in the compound to the gas phase and deposit them at another temperature. Sulfides with a phase range, such as FeS$_x$, can be transported systematically as well [18 – 20, 152]. Mixed-crystals with substitution in the cationic sublattice, such as Co$_{1−x}$Fe$_x$S [153]; in the anionic sublattice, such as TiS$_{2−x}$Se$_x$ [154 – 156]; or in the cationic *and* anionic sublattice, such as Ge$_x$Pb$_{1−x}$S$_{1−y}$Se$_y$ [157] are accessible with defined compositions and in crystalline form. Here, sulfides and selenides behave in very similar ways. This is because of the similar ionic radii of the sulfide and selenide ions and the same electronegativity. Both properties cause similar chemical behavior and similar thermodynamic stabilities. Thus often the metal sulfides and selenides have the same structure types. Additionally, sulfides

and selenides are often mixable completely in the solid state. Thus, the essential aspects that apply for the transport of sulfides, also apply for the selenides.

While heating, most of the metal sulfides decompose completely or partly to the elements. If the metal has a sufficiently high vapor pressure at the decomposition temperature, one can observe in some cases a *decomposition sublimation* (152).

$$MS(s) \rightleftharpoons M(g) + 1/2\, S_2(g) \tag{152}$$
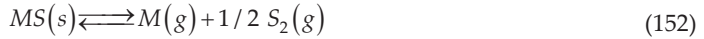
($M$ = Zn, Cd)

Only a few metal sulfides can be sublimed undecomposed. Examples are gallium(I) sulfide, germanium(II) sulfide, tin(II) sulfide, lead(II) sulfide:

$$Ga_2S(s) \rightleftharpoons Ga_2S(g) \tag{153}$$

$$MS(s) \rightleftharpoons MS(g) \tag{154}$$

($M$ = Ge, Sn, Pb)

Some sulfides decompose to a metal-rich solid and gaseous sulfur, for example pyrite, which forms FeS(s) and $S_2$(g) (155) at high temperatures. In some cases, the metal-rich sulfides, which were formed by thermal decomposition, can appear in the gas phase as well. These compounds show noticeable effects of the gas phase transport by decomposition sublimation (156).

$$FeS_2(s) \rightleftharpoons FeS(s) + 1/2\, S_2(g) \tag{155}$$

$$MS_2(s) \rightleftharpoons MS(g) + 1/2\, S_2(g) \tag{156}$$
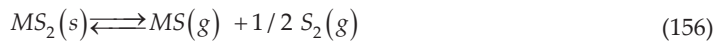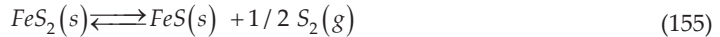
($M$ = Si, Ge)

**Transport of sulfides with iodine as transport agent**. Mainly iodine is used as the transport agent for sulfides (as for selenides and tellurides). During the CVT of sulfides with iodine or iodine compounds, the corresponding metal iodide and sulfur are generally formed as transport effective species. In the temperature range that is often used for transport reactions (around 800 to 1000 °C), sulfur is mostly present as the $S_2$-molecule. At lower temperatures, the formation of larger sulfur molecules ($S_2$, $S_3$ … $S_8$) is additionally expected. The CVT of homogeneously composed crystals of sulfide-selenide solid solutions succeeds by similar vapor pressures of the respective selenium gas species ($Se_2$,… $Se_8$). In this respect, the system of cubic mixed-phases ZnS/SnSe has been examined in detail. Zinc sulfide and zinc selenide are completely mixable in the solid state and, moreover, can be transported under the same conditions. Consequently, the transport of $ZnS_{1-x}Se_x$ by adding iodine [158] results in large

crystals without significant changes of the composition between source and sink [159], Figure 26. The concentration effects become clear by thermodynamic modeling of $ZnS_{1-x}Se_x$ mixed-phases and their transport behavior [159].
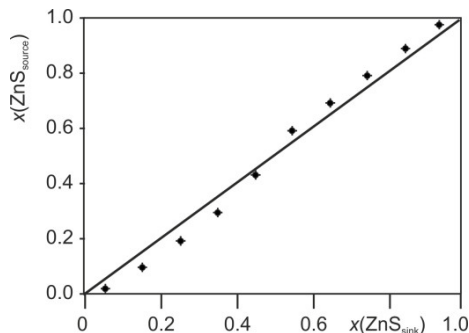


**Figure 26.** Relation between the composition of the solid in the source and sink during the transport of $ZnS_{1-x}Se_x$ mixed phases with iodine, according to [159].

The crystallization of iron(II) sulfide plays an important role for the understanding of vapor transports for compounds with a considerable homogeneity range. The transport of "FeS" with iodine was already reported in early times [1, 8, 160, 161]. Nevertheless, the transport does not always succeed under the given conditions, as it is dependent on the composition of the initial solid $FeS_x$, too [18]. When iodine is added, the gas phase over $FeS_x$ basically contains $FeI_2$, $Fe_2I_4$, $FeI_3$, I, $I_2$, and $S_2$. Their partial pressures are dependent on the temperature and the composition of the solid, Figures 27, 28. Thus, at 1000 °C, sulfur is volatized in noteworthy scale only for solids of iron sulfide with $x > 0.05$ but the sulfur pressure is very low for stoichiometrically composed $FeS_{1.0}$. Consequently, due to the insufficient amount of sulfur as transport effective species, the transport of $FeS_{1.0}$ using iodine is not possible [18, 19].
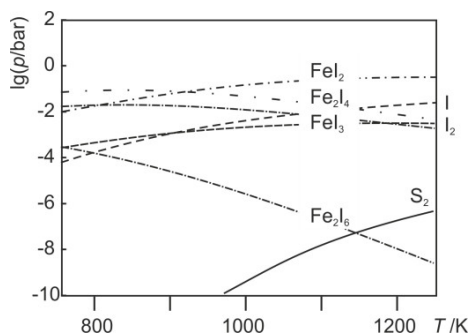


**Figure 27.** Composition of the gas phase for the transport of $FeS_{1.0}$ using iodine, according to [2, 18].
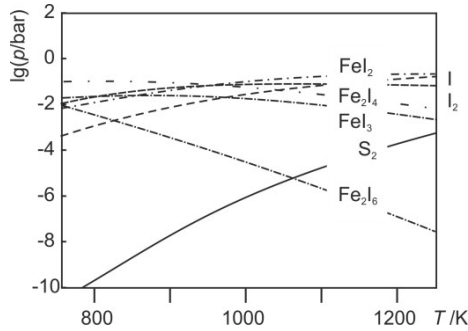
**Figure 28.** Composition of the gas phase for the transport of $FeS_{1.1}$ using iodine, according to [2, 18].

**Transport of sulfides with addition of hydrogen halides.** However, the transport of $FeS_{1.0}$ succeeds with hydrogen halides as transport agents (HCl, HBr, HI). In these cases, sulfur is not present in the gas phase in elemental form but as $H_2S$. Thus the solubility of sulfur increases by some orders of magnitude, and the transport succeeds with transport rates of some milligrams per hour [20]. The transport of hydrogen halide can be advantageous for sulfur-poor compounds when there is no transport effective solution due to the low partial pressure of sulfur.

$$FeS(s) + 2\,HCl(g) \rightleftharpoons FeCl_2(g) + H_2S(g) \tag{157}$$
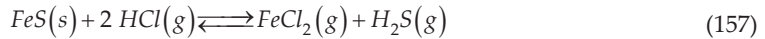
The use of hydrogen chloride was even successful to optimize the transport behavior of mixed-crystals $ZnS_{1-x}Se_x$ [162, 163]. Instead of pure HCl ammonium chloride, $NH_4Cl$, can be used as an additive. Then, hydrogen chloride is formed during heating of the transport ampoule.

$$ZnS_{1-x}Se_x + 2\,HCl(g) \rightleftharpoons ZnCl_2(g) + (1-x)\,H_2S(g) + xH_2Se(g) \tag{158}$$
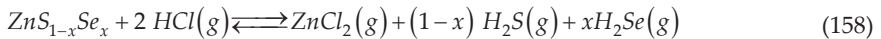
A series of studies report the CVT reactions of sulfides with halogenating additives $CrCl_3$, $AlCl_3$, $CdCl_2$, or $TeCl_4$. At least for transports with $AlCl_3$ and $TeCl_4$ the formation of hydrogen chloride (159) as an effective transport agent can be expected, too.

$$2\,AlCl_3(g) + 3\,H_2O(g) \rightleftharpoons Al_2O_3(s) + 6\,HCl(g) \tag{159}$$
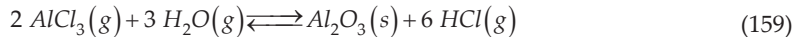
**Transport of sulfides with hydrogen and other elements as transport agents**. During a few transport reactions, the transport agent does not react with the metal atoms of the solid but with the sulfur atoms instead. In particular, hydrogen is one of these transport agents, which can be used successfully for cadmium and zinc compounds. Transport reactions in which

hydrogen is used as transport agent are unusual. Here, the transport agent reacts with sulfur atoms of the solid under formation of hydrogen sulfide [164]. The vapor transports are made possible by the fact that zinc and cadmium, respectively, can be formed elementally in gaseous form during these reactions. The transport with hydrogen is also suited to grow larger single-crystals [165, 166], compared to iodine. Additionally, the contamination of the obtained crystals by transport agent is excluded.

$$CdS(s) + H_2(g) \rightleftharpoons Cd(g) + H_2S(g)$$
(160)
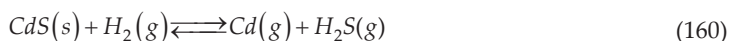
Transport reactions in which the transport agent reacts solely with the non-metal of the solid are exceptions. Thus, for the transport of zinc sulfide with phosphorus gaseous PS is formed [167].

$$CdS(s) + 1/4 \, P_4(g) \rightleftharpoons Cd(g) + PS(g)$$
(161)
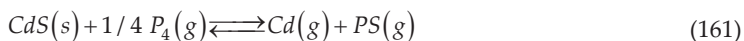
In some cases ($SiS_2$, $TiS_2$, $TaS_2$), CVT with sulfur as transport additive was successful. The transport effect was ascribed to the formation of gaseous polysulfides [168].

**Transport of selenides and tellurides**. To date, many examples of CVT of selenides and tellurides of the main group elements (groups 2, 13, 14, and 15) as well as almost all transition metal elements are known; some lanthanoids are included, too [2]. The first reports of on the preparation and purification of selenides and tellurides coincide with the methodological development of the CVT [150]. The alkali metal selenides and tellurides cannot be transported with halogens or halogen compounds due to their high stability. As the selenides and even more the tellurides are less stable than the analogous sulfides, the transport reactions are less endothermic. As a consequence higher partial pressures of the transport effective species and lower temperatures of volatilization, respectively, can be applied. Some selenides and tellurides sublime undecomposed. This applies for the compounds of groups 13 and 14, $MQ$ ($M$ = Ge, Sn, Pb, $Q$ = Se, Te) and $M_2Q$ ($M$ = Ga, In, Tl), respectively. A vast number of compounds show noticeable effects of dissolution by decomposition reactions in the gas phase. In the process, high volatile chalcogen-poor chalcogenides as well as the gaseous chalcogen are formed (162 – 164).

$$M_2Q_3(s) \rightleftharpoons M_2Q(g) + Q_2(g)$$
(162)

($M$ = Al, Ga, In)

$$GeSe_2(s) \rightleftharpoons GeSe(g) + 1/2 \, Se_2(g)$$
(163)

$$n/2\, M_2Q_3(s) \rightleftharpoons M_nQ_n(g) + n/4\, Q_2(g) \tag{164}$$
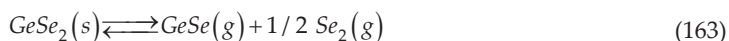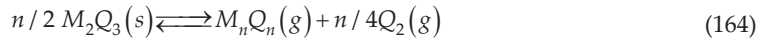
($M$ = As, Sb, Bi)

The thermal decomposition of ZnSe and CdSe (and similarly ZnTe, CdTe, HgTe) to the elements is of importance, too. Applying the decomposition equlibria (165), the deposition of crystalline ZnSe and CdSe over the gas phase is possible at temperatures above 1000 °C ($Kp >$ $10^{-4}$ bar) without adding a transport agent. Thus the thermodynamic basis of physical vapor deposition (PVD) processes for deposition of layers of these two compounds is provided [169 – 171].

$$MSe(s) \rightleftharpoons M(g) + 1/2\, Se_2(g) \tag{165}$$
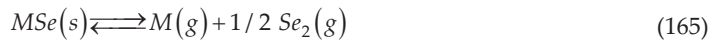
($M$ = Zn, Cd)

More than three quarters of all known CVT reactions of selenides and tellurides take place with the addition of iodine. At temperatures above 600 °C, $Se_2$ dominates in the gas phase (166). Below this temperature, the higher condensed molecules $Se_n$ ($n$ = 3 … 8) have to be considered. The transport of tellurides dominantly runs by formation of $Te_2$ as effective species.

$$CdSe(s) + I_2(g) \rightleftharpoons CdI_2(g) + 1/2\, Se_2(g) \tag{166}$$

Besides transports by using hydrogen or hydrogen halides have been reported.

$$MnSe(s) + 2\, HCl(g) \rightleftharpoons MnCl_2(g) + H_2Se(g) \tag{167}$$

$$ZnSe(s) + H_2(g) \rightleftharpoons Zn(g) + H_2Se(g) \tag{168}$$
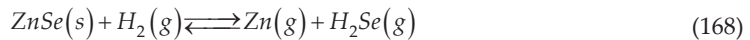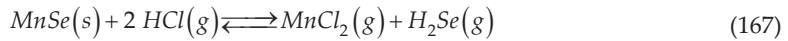
As already mentioned, the use of hydrogen or hydrogen halides as transport agent is important for the transport of oxides and sulfides because the solubility of oxygen and sulfur, respectively, in the gas phase is supported by the formation of water and hydrogen sulfide, respectively. However, the stability of hydrogen compounds $H_2Q$ ($Q$ =O, S, Se, Te) constantly decreases, the participation of $H_2Se$ and, in particular, of $H_2Te$ in CVT reactions must be discussed critically. $H_2O$ as well as $H_2S$ is still stable above 1000 °C. $H_2Se$, however, decomposes already between 700 and 800 ° ($Kp_{,1000}(H_2Se)$ = 1 bar). $H_2Te(g)$ is unstable in the entire temperature range ($Kp_{,T}(H_2Te)$ = $10^2$ bar), Figure 29. Consequently, the partial pressure of $Te_2(g)$ resulting from the equilibrium (169) is higher by orders of magnitude. Accordingly, the described transport of cadmium telluride in the presence of hydrogen [172, 173] should rather be seen as a decomposition sublimation. Transport reactions that take place with added

halogen/hydrogen mixtures occur under formation of the respective metal halides and $Te_2$ (170), [172 – 174].

$$2/3\,H_2Q(g)\Longleftrightarrow 2/3\,H_2(g)+1/3\,Q_2(g) \tag{169}$$

($Q$ = O, Se, Se, Te)

$$MTe(s)+2\,HX(g)\Longleftrightarrow MX_2(g)+H_2(g)+1/2\,Te_2(g) \tag{170}$$
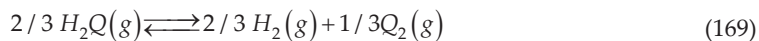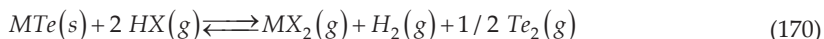
($M$ = Cd, Pb, Zn)
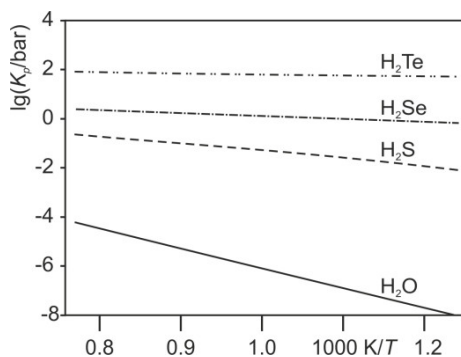


**Figure 29.** Equilibrium constants $K$p for the decomposition of hydrogen chalcogenides $H_2Q$ ($Q$ = O, S, Se, Te) in equilibrium (169), according to [2].

### 3.2.7. Chemical vapor transport of pnictides

The character of chemical bonding of metal pnictides is very variable and ranges from the metallic, ionic, and covalent nitrides and phosphides through the rather covalent or metallic arsenides and antimonides to the typical metallic bismutides. Thus the transport behavior changes significantly. There is only one example of the CVT of a binary nitride, TiN [175]. The chemical vapor transport of phosphides and arsenides is documented by numerous examples [2] while there are only a few examples of the transport of antimonides and only one of a bismuth-containing intermetallic phase, NiBi [176].

Elemental halogens, in particular iodine, and halogen compounds are preferred as transport additives. While nitrogen, phosphorus, and arsenic have sufficiently high saturation pressures to be transport effective in elemental form, it is necessary to generate transport- effective compounds for the antimonides and bismuthides. This becomes possible by the increasing tendency of pnicogens to form halogen compounds. Concerning the transport of phosphides, in the gas phase mostly phosphorus(III) halides occur. For the transport of arsenides and

**Figure 30.** Crystal of ZrAs$_2$ grown by chemical vapor transport.

antimonides one has to expect, at rising temperatures, the formation of monohalides, too. This applies in particular for the heavy halogens.

**Transport of phosphides with iodine as transport age**nt. In most cases, the transport of phosphides of the transition metals by adding iodine is possible. As a special feature, transports of phosphides require a comparatively high transport agent density of iodine of about 5 mg cm$^{-3}$. Depending on the thermodynamic stability of the phosphide and the volatile metal iodide, the vapor transport can occur in a temperature gradient via exothermic (e. g., VP (171), MnP, Cu$_3$P (172)) or endothermic (e. g., CrP (173), CoP (174), CuP$_2$) reactions [2]. The addition of phosphorus(III) iodide and hydrogen iodide as transport agent induces similar transport reactions (175, 176).

$$VP(s) + 7/2\ I_2(g) \rightleftharpoons VI_4(g) + PI_3(g) \tag{171}$$

$$Cu_3P(s) + 3\ I(g) \rightleftharpoons Cu_3I_3(g) + 1/4\ P_4(g) \tag{172}$$

$$CrP(s) + I_2(g) \rightleftharpoons 1/2Cr_2I_4(g) + 1/4\ P_4(g) \tag{173}$$

$$CoP(s) + 5/2\ I_2(g) \rightleftharpoons CoI_2(g) + PI_3(g) \tag{174}$$

$$CuP_2(s) + 1/3\ PI_3(g) \rightleftharpoons 1/3\ Cu_3I_3(g) + 7/12\ P_4(g) \tag{175}$$

$$MnP(s) + 2\ HI(g) \rightleftharpoons 1/2\ Mn_2I_4(g) + 1/4\ P_4(g) + H_2(g) \tag{176}$$
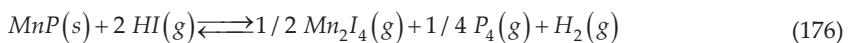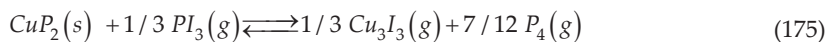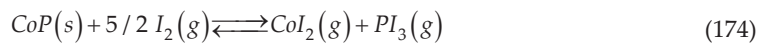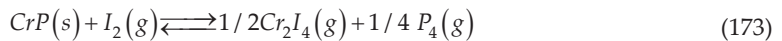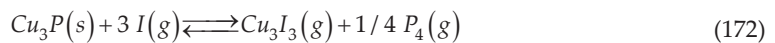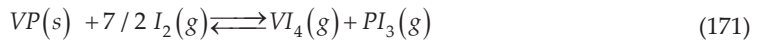
Experimental results suggest that phosphides show the best results (high transport rates; large crystals) at a ratio of $n(M) : n(P)$ close to 1 : 1. Chemical vapor transports of metal-rich and phosphorus-rich phosphides can only be conducted with lower efficiency. This is due to the unbalanced chemical activities of the components in the respective binary compounds: If the activity of the metal component in a phosphide is high but that of phosphorus very low (metal-rich phosphide), the only reaction that will occur is that of the transport agent iodine with the metal under formation of the volatile metal iodide. In some cases, even its saturation pressure is exceeded so that condensed metal iodides appear as well. Phosphorus is kept and enriched in the solid; the simultaneous volatilization of both components is impossible. The reactions of $Cr_{12}P_7$, $Fe_2P$, and $Co_2P$ with iodine can be served as examples of this behavior [138]. Otherwise, the formation of very stable metal iodides, as described above, can lead to the development of phosphorus-rich phosphides (incongruent volatilization of phosphides) even without high metal activity in a phosphide. Thus in experiments with sufficiently high initial amounts of iodine $TiP_2$ adjacent to TiP [177]; $ZrP_2$ adjacent to ZrP [177]; as well as $CuP_2$ adjacent to $Cu_3P$ and CuI(l) [178] appeared (177, 178).

$$2MP(s) + 2\,I_2(g) \rightleftarrows MI_4(g) + MP_2(s) \tag{177}$$

($M$ = Ti, Zr)

$$2\,Cu_3P(s) + 5/2\,I_2(g) \rightleftarrows 5\,CuI(l) + CuP_2(s) \tag{178}$$
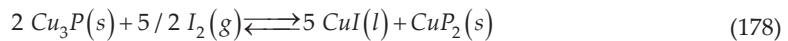
**Transport of phosphides with mercury bromide as transport agent**. If the phosphorus coexistences pressure is too low to be transport effective and additionally does the thermodynamic stability of the phosphorus iodides $P_2I_4$ and $PI_3$ not suffice to keep phosphorus in the gas phase, $HgBr_2$ can be applied as transport agent. Thus for metal-rich phosphides, $Mo_3P$, $Mo_4P_3$, and $Fe_2P$, the transfer of phosphorus through the gas phase takes place via the more stable phosphorus bromide (179-181) [138, 179].

$$Mo_3P(s) + 9/2\,HgBr_2(g) \rightleftarrows 3\,MoBr_2(g) + PBr_3(g) + 9/2\,Hg(g) \tag{179}$$

$$Mo_4P_3(s) + 17/2\,HgBr_2(g) \rightleftarrows 4\,MoBr_2(g) + 3\,PBr_3(g) + 17/2\,Hg(g) \tag{180}$$

$$Fe_2P(s) + 7/2\,HgBr_2(g) \rightleftarrows 2\,FeBr_2(g) + PBr_3(g) + 7/2\,Hg(g) \tag{181}$$
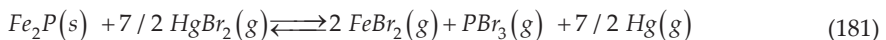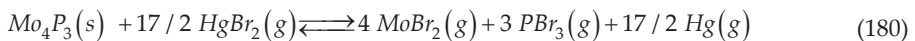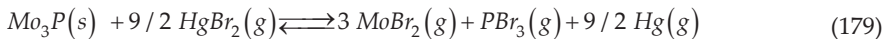
**Transport of phosphides with phosphorus**. In contrast to the above discussed transport reactions of phosphides with halogens or halogen compounds, the transport of InP and GaP

succeeds by adding an excess of phosphorus. *Ab initio* calculation of the stability of different gas species in the system are indicating the formation of $MP_5(g)$ (*M*: In, Ga) [180].

$$MP(s) + P_4(g) \rightleftharpoons MP_5(g) \tag{182}$$

(*M* = In, Ga)

**Transport of arsenides**. The CVT of arsenides is referred for many examples [2]. Because of the technical applications of gallium arsenide, the arsenides of group 13 are experimentally examined in a comprehensive manner. Compared to the other pnictides, the transport of arsenides behaves similar to that of phosphides but markedly different to those of the anti-monides and bismutides. This is due to the high saturation vapor pressure of phosphorus and arsenic at rather low temperatures: 1 bar at 277 °C and 602 °C, respectively. Hence phosphorus as well as arsenic can be transferred to the gas phase in considerable amounts at relatively low temperatures without exceeding the saturation vapor pressure and thus condensing again. The saturation vapor pressure of antimony, in contrast, reaches the value of 1 bar at 1585 °C. As far as the thermodynamic stability of the pnictides is concerned, phosphides and arsenides are similar as well. Consequently, the most important transport agent for the crystallization of the arsenides is iodine as well (183).

$$NdAs(s) + 3\,I(g) \rightleftharpoons NdI_3(g) + 1/2\,As_2(g) \tag{183}$$
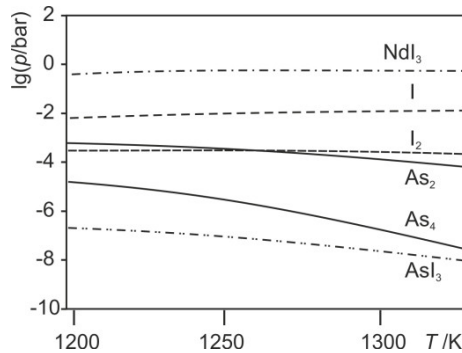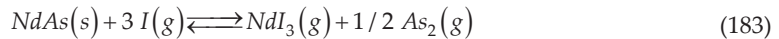


**Figure 31.** Composition of the gas phase for the transport of NdAs using iodine, according to [2].

Thermodynamic model calculations make clear, that the *transport additive* iodine (or other halogens), not necessarily acts as the effective *transport agent*. Often the arsenic trihalides or the metal or semi-metal halides, respectively, which are formed from the halogens and the solids, function as such. In the transport equilibria of FeAs (184) and GaAs (185), iodine is added but arsenic(III) iodide is the effective transport agent.

$$FeAs_2(s) + AsI_3(g) \rightleftharpoons FeI_2(g) + 3/4\ As_4(g) + 1/2\ I_2(g) \tag{184}$$

$$GaAs(s) + 1/2\ GaI_3(g) \rightleftharpoons 3/2\ GaI(g) + 1/4\ As_4(g) \tag{185}$$
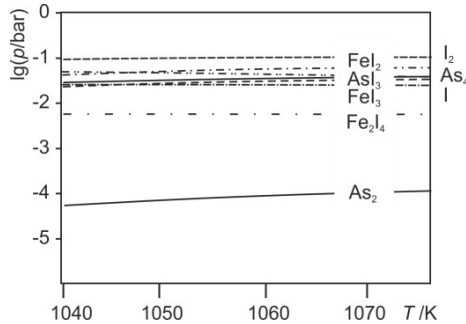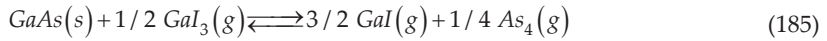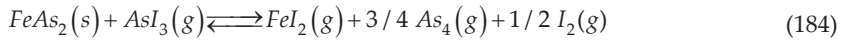


**Figure 32.** Composition of the gas phase for the transport of FeAs$_2$ using iodine, according to [2].

Arsenic is transferred into the gas phase mainly in elemental form due to the high saturation pressure and the comparatively low stability of gaseous arsenic iodides. Up to approximately 900 to 1000 °C the gas phase is mostly dominated by As$_4$, above that temperature by As$_2$. The species As$_3$ and As are of minor importance to the CVT.

The endothermic transport of silicon arsenide, SiAs can be described by the formation of SiI$_4$ as effective transport agent (186).

Otherwise, an exothermic transport can be described by HI as transport agent (187), which is formed by traces of water desorbed off the ampoule walls [181].

$$SiAs(s) + SiI_4(g) \rightleftharpoons 2\ SiI_2(g) + 1/4\ As_4(g) \tag{186}$$

$$SiAs(s) + 4\ HI(g) \rightleftharpoons SiI_4(g) + 1/4\ As_4(g) + 2H_2(g) \tag{187}$$
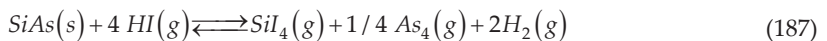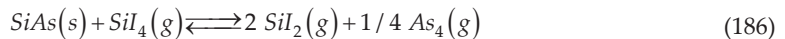
Additionally, hydrogen halides, hydrogen chloride in particular, are important for the transport of arsenides of group 13 (BAs, GaAs, and InAs). The transport of gallium arsenide with hydrogen chloride (188) and hydrogen bromide, respectively, is well investigated experimentally and by thermodynamic calculations. Here, the formation of AsH$_3$ has to be taken into account for complex description of the transport behavior. Additionally, GaAs, InAs, Ga$_{1-x}$In$_x$As and InAs$_{1-x}$P$_x$ can be transported with water. The transport occurs via the equilibrium (189):

$$GaAs(s) + HX(g) \rightleftharpoons GaX(g) + 1/4\ As_4(g) + 1/2\ H_2(g) \tag{188}$$

($X$ = Cl, Br)

$$2\ GaAs(s) + H_2O(g) \rightleftharpoons Ga_2O(g) + As_2(g) + H_2(g) \tag{189}$$
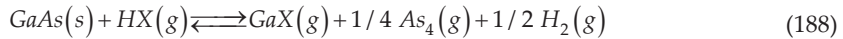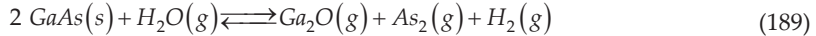
The transport reaction is always coupled with a redox equilibrium in which a gaseous suboxide [182], arsenic, and hydrogen are formed. Finally, GaAs can be transported with a mixture of water and hydrogen. The mentioned transport agents are used especially in open systems with flowing gases [183].

## 4. Advanced concepts and thermodynamic modeling of CVT

The course of chemical vapor transports can be understood by thermodynamic considerations (see chapter 2.2). Here various thermodynamic models will be explained in detail. It is state-of-the-art to use computer programs for modeling and quantitative description of transport reactions. Thus, optimum experimental conditions, the direction of a transport, and transport rates can be obtained for many transport systems, frequently even in a predictive way. For more complicated cases, however, a detailed treatment of the underlying thermodynamics will be required. Such a treatment is particularly necessary when a condensed phase with homo-geneity range or multi-phasic equilibrium solids do occur in a transport experiment. In addition to the influence of thermodynamic data and phenomena, the transport behavior can be affected by kinetic effects. While the mass flow via the gas phase is generally assumed to be rate determining, some examples have been observed where the kinetics of one or more elementary reaction steps in the transport process exert a dominating influence.

In all cases, the simple looking as well as the more complicated ones, prior to an experiment the experimenter has to develop some idea of which condensed equilibrium phases and gaseous species are to be expected for the transport system under consideration. This knowl-edge is an essential prerequisite if modeling of transport experiments is to have an outcome close to reality. The most important characteristics for various transport processes are sum-marized by the following schematics.

**Congruent vaporization of a condensed phase**: The ratio of the elements in the condensed phase and the gaseous phase of the source are identical. Because of the congruent dissolution of all components into the gas phase always a congruent deposition at the sink occurs. Thus a stationary (steady state), not time-dependent transport behavior result.

*The model of simple transport behavior:* The vapor transport process can be fully described by a *single* heterogeneous equilibrium reaction. The assessment of the equilibrium state can be realized by calculation of $Kp$ and subsequently of $\Delta p$ (see chapter 2.2). Hence, the estimation of the transport direction succeeds using the sign of $\Delta_r H^0$ ($\Delta_r H^0 > 0$, $T_2 \rightarrow T_1$ or $\Delta_r H^0 < 0$, $T_1 \rightarrow T_2$).

*The model of complex transport behavior* The gas-phase composition is formed by *several* independent equilibria. The assessment of the equilibrium state requires the calculation of the gas phase solubility $\lambda$ of regarding components, see section 4.1. Consequently, the change of solubility $\Delta\lambda$. describes the direction of the transport ($\Delta\lambda_{\text{T2-T1}} > 0$, $T_2 \rightarrow T_1$; $\Delta\lambda_{\text{T2-T1}} < 0$, $T_1 \rightarrow T_2$).

**Incongruent dissolution of the source's condensed phase in the gas phase**: During an incongruent dissolution, the molar ratio of the elements in the condensed phase and in the gas phase of the source are not identical. This behavior is always caused by simultaneous occurrence of *several* independent equilibria. In this case the calculation of the mass flow of the components *A* and *B*, *J(A.B)*, between the equilibrium regions (volumes) is of decisive importance. Hence, the transport is to describe by the *flux relation*.

*The extended transport model*: This thermodynamic model represents the "quasi-stationary transport" behavior. Thereby, constant phase relations and equilibrium conditions are assumed. Actually, this assumption only applies for the first moment of the experiment. Nevertheless, the thermodynamic description by extended transport model fits very well, if time-independent behavior is experimentally observed. The determination of the composition of the sink's condensed phase succeeds by applying the condition for steady state with $\varepsilon$ = constant ($\varepsilon$: relation of stationarity).

*The co-operative transport model*: If the composition of the deposited solid at the sink changes time-dependently it is called a "sequential transport". This non-stationary transport behavior can be described by the co-operative transport model. The determination of the composition of the sink's condensed phases and of the deposition sequence is realized by an iteration procedure.

## 4.1. Complex congruent transports

There are many examples, where chemical transport of a solid cannot be completely described by *just one* reaction, since a more complex gas phase is formed. For these cases several unique equilibrium reactions have to be considered. Their number $r_u$ has to be derived by using equation (190). Here, *s* is the number of gas species, *k* the number of components (according to Gibbs's phase rule the number of elements).

$$r_u = s - k + 1 \tag{190}$$

The transport of iron with iodine corresponding to van Arkel [5, 6] might serve as an example for complex congruent transport behavior. The gas species $FeI_2$, $Fe_2I_4$, $I_2$, and I might occur. According to $r_u = 4 - 2 + 1 = 3$ the partial pressures of all gas species are determined by three unique equilibria (191 - 193).

$$Fe(s) + I_2(g) \rightleftharpoons FeI_2(g) \tag{191}$$

$$2\,Fe(s) + 2\,I_2(g) \rightleftharpoons Fe_2I_4(g) \tag{192}$$

$$I_2(g) \rightleftharpoons 2\,I(g) \tag{193}$$

The first transport equilibrium (191) is endothermic ($\Delta_r H^0_{298} = 24\,kJ \cdot mol^{-1}$). According to Le Chatelier's principle, a transport from $T_2$ to $T_1$ is expected. Reaction (192) has the character of a transport equation, too. This reaction runs exothermic ($\Delta_r H^0_{298} = -116\,kJ \cdot mol^{-1}$). The situation becomes even more complicated because iodine is present partly in atomic form at high temperatures (193). Applying atomic iodine, further transport reactions under the formation of $FeI_2(g)$ and $Fe_2I_4(g)$ can be formulated. In all cases the molecules $FeI_2$ and $Fe_2I_4$ function as transport effective species. Thus, below 1000 °C, we deal with two opposing processes – the increasing formation of $FeI_2$ and the decreasing formation of $Fe_2I_4$, both because of rising temperature. The first process lets us expect transportation towards the cooler zone, the second one to the hotter zone. It is not predictable which process dominates. A new term – the **gas phase solubility** [15] – is helpful for answering this question.

**The gas phase solubility**. The term gas phase solubility $\lambda$ refers back to the term solubility of a substance in a liquid. Solutions of solid substances are used for the purification of the dissolved substance through recrystallization. One uses the temperature dependency of the solubility, respectively the solubility equilibrium, and produces an in heat saturated solution. Through cooling, a recrystallization of the solid substance is achieved. A chemical vapour transport reaction works basically the same way. Here, one also uses the temperature dependency of the equilibrium position of the reaction in order to crystallize and to purify. In both cases, one deals with heterogeneous equilibria; in the first case between a solid and a liquid, in the second between a solid and a gas phase [15].

The example of the transport of iron shows the advantage of the term solubility in the description of complicated transport reactions. According to the transport equations (191) and (192), iron can be solved into the gas phase forming the species $FeI_2$ and $Fe_2I_4$. The solvent is the gas phase, i.e. all gaseous species together. The quantitative description of the solubility of iron in the gas phase considers that one molecule $Fe_2I_4$ includes two Fe-atoms, whereas the $FeI_2$ molecule only includes one. Hence the partial pressure of $Fe_2I_4$ is multiplied by the factor 2. If analogously same applies to the solvent gas phase, the solubility of iron in the gas phase can be described by equation (194):

$$\lambda(\text{Fe}) = \frac{p(\text{FeI}_2) + 2 \cdot p(Fe_2I_4)}{p(\text{I}) + 2 \cdot p(\text{I}_2) + 2 \cdot p(\text{FeI}_2) + 4 \cdot p(Fe_2I_4)} \tag{194}$$

The temperature dependency of the solubility of iron in the gas phase takes both ferrous molecules $FeI_2$ and $Fe_2I_4$ into consideration. Figure 33. As the solubility of iron decreases with growing temperatures, less iron is dissolved at higher temperatures in the gas phase

than at lower temperatures. Thus iron must be transported from lower to higher tempera-
tures. This is in accordance with experimental observations of iron transport with iodine
from 800 to 1000 °C.
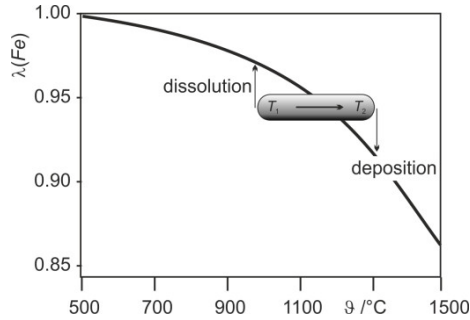


**Figure 33.** Temperature dependence of the solubility of iron and direction of the transport, according to [2].

**Conclusion**. With the aid of *solubility of a solid in the gas phase* several possible transport
reactions including a variety of gas species can be considered for a complex transport system.
The solubility $\lambda$ can be described by the expression $\lambda = n^*(A)/n^*(L)$ or, using the relation
between $n$ and $p$ given by the ideal gas law, by $\lambda = p^*(A)/p^*(L)$. $L$ is meaning the solvent, which
can be the transport agent or even an inert gas. The balance of $A$ and $L$ is expressed by the sum
of all involved species (195). The numbers $\nu(A)$ and $\nu(L)$ denominate the stoichiometric
coefficients of $A$ and $L$ in the gas species. The equation (195) for the solubility of a solid in a
gas phase holds for systems of any order of complexity in closed as well as in open systems.

$p * (A) = \Sigma(\nu(A) \cdot p(A))$

$$\lambda(A) = \Sigma(\nu(A) \cdot p(A)) / \Sigma(\nu(L) \cdot p(L)) \tag{195}$$

Given that equilibrium has been established, the transport direction depends on the difference
$\Delta\lambda$ (196):

$$\Delta\lambda = \lambda(T_2) - \lambda(T_1) \tag{196}$$

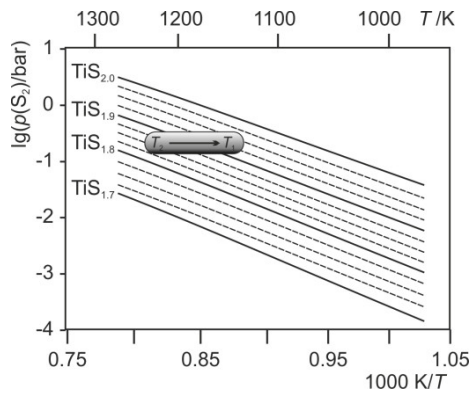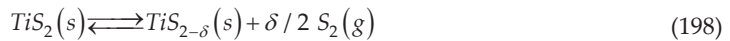$\Delta\lambda > 0$ transport direction $T_2 \rightarrow T_1$

$\Delta\lambda < 0$ transport direction $T_1 \rightarrow T_2$

### 4.2. Incongruent stationary transports (Extended transport model)

The thermodynamic description and modeling of transport systems get increasingly compli-
cated if the transported compound shows a homogeneity range $AB_{x\pm\delta}$ or the transport occurs

in a system with several coexisting condensed phases, e. g. $AB_y$ and $AB_z$. Their vapor transports rather often occur under incongruent dissolution. This case is characterized by different molar ratios of the components (elements) in the source solid and the corresponding gas phase. Consequently, the ratio $(n(B)/n(A))$ of the solid $AB_{x,\,T(sink)}$ is not longer identical to the ratio of the balance pressures $p^*(A)/p^*(B)$ of the components $A$ and $B$ at the sink. Hence, the ratio of the components of the deposited phase (at the sink) does not need to be identical to that of the dissolved phase (source). This behavior is comparable to the peritectic melting of a solid and the compositional shift that accompanies the re-formation of a solid from this melt upon cooling. The composition of melt and solid are different.

The general task to describe transport reactions with phases of variable composition can be treated in a vivid way for the transport within the homogeneity range of $TiS_{2-\delta}$ [16]. The actual transport equilibrium (197) is attended by the decomposition reaction (198).

$$TiS_{2-\delta}(s) + 2\,I_2(g) \rightleftharpoons TiI_4(g) + (2-\delta)/2\,S_2(g) \tag{197}$$

$$TiS_2(s) \rightleftharpoons TiS_{2-\delta}(s) + \delta/2\,S_2(g) \tag{198}$$
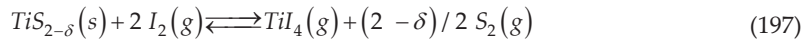


**Figure 34.** Phase barogram for the system Ti/S showing the co-existence pressures (according to 198) in the homogeneity range $TiS_{2-\delta}$. The phase relations in CVT experiments (950 to 850 °C) are visualized; graphic according to [16, 2].

For transport experiments in the temperature gradient 950 to 850 °C, independent on the starting composition $TiS_{2-\delta}$ of the source solid, at $T_1$ a sulfur-enriched phase will always be deposited. At the same time a sulfur-depleted phase forms at the source. Thus, the vapor transport starting from an initial composition $TiS_{1.889}$ yields crystals of $TiS_{1.933}$. Consequently, the solid at the source is depleted of sulfur, see Figure 34. The thermodynamic description of the observed phase relations is possible in a rather simple approach by independent calculation of the equilibrium conditions for source and sink. As both equilibrium regions are linked to each other via the gas phase, solids of corresponding compositions are obtained

at $T_2$ and $T_1$ with the precondition $p(S_2)$ = constant (above $TiS_{2-\delta1}$ at $T_1$ and $TiS_{2-\delta2}$ at $T_2$; $\delta_2 <$ $\delta_1$). Using the phase barogram ($\lg(p/p^0) = f(x, T)$) of the corresponding system the determination of the stoichiometric coefficients $x$ succeeds along an isobar for given temperatures $T_2$ and $T_1$ (Figure 34).

A farther-reaching, general treatment of the phase relations encountered in transport systems with incongruent dissolution of a solid is based on the fact that the two equilibrium regions (source and sink) are indeed not independent to each other: In a system of two components $A$ and $B$, the solid $AB_x$ will be transferred by the transport agent $X$ into the gas phase. According to Gibbs' phase rule the system with three components and two phases (solid+gas phase) possesses three degrees of freedom for its thermodynamic description: $\Delta p$, $T_{source}$, and $x(_{Tsource})$

$$AB_{x,source}(s) + X(g) \rightleftarrows AX(g) + x\ B(g) \tag{199}$$
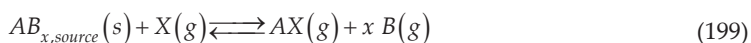
$$F = C - P + 2 \rightarrow F = 3 - 2 + 2 = 3$$

From the considerations follows that the composition of $AB_{x,sink}$ at the sink temperature $T_{sink}$ might be variable, but not independent of the equilibrium conditions valid for the dissolution (source) region ($T_{source}$, $x_{source}$, $\Delta p$). For a congruent chemical vapor transport, modeling of the transport effect is possible via *independent equilibrium calculations* for source and sink region followed by determination of the differences of partial or balance pressures. In contrast to this situation the equilibrium calculations for source and sink of an incongruent transport have to be linked to each other. Only in doing so, it becomes possible to determine the composition $AB_{x,\ sink}$ at $T_{sink}$. The relation between the two equilibrium regions at $T_{source}$ and $T_{sink}$ can be described by the mass flow via the gas phase from source to sink. Thereby, not the total substance amounts $n(A)$, $n(B)$ are considered but the resulting differences of the molar numbers in the gas phases of source and sink $n_{source} - n_{sink}$. As a consequence, the composition of $AB_{x,sink}$ is determined by the ratio of the molar flow for $A$ and $B$, but not by the ratio of the balance pressures (200)

$$\left(\frac{n(B)}{n(A)}\right)_{T_{sink}} = \left(\frac{flux(B)}{flux(A)}\right)_{T_{source} \rightarrow T_{sink}} = \left(\frac{J(B)}{J(A)}\right) = x_{sink} \tag{200}$$

For a congruent transport equation (200) is valid, too. Obviously, a transfer with constant molar ratio of the components will occur between the equilibrium regions if the ratio of the balance pressures between source and sink is constant. The validity of the flux relation is assumed for *all* chemical transport reactions. The steady-state is given for an incongruent transport only as long as the equilibrium state at the source remains constant. For different values of $x_{sink}$ and $x_{source}$, the composition of the source solid and the sources gas phase have to change during the course of the transport experiment. The compositional change of the source solid might proceed by discontinuous compositional change by formation of two co-existing phases or continuous compositional change within a homogeneity range.

According to Krabbes, Oppermann, and Wolf the steady-state of a transport system involving incongruent dissolution of a solid $AB_x$ is determined by linking the balance of molar numbers for $A$ in the sink [$n(A(s))_{sink}+n(A(g))_{sink}$] to the molar number of $A$ in the gas phase of the source [18 - 21]. The molar number of $A$ in the sources solid does obviously not contribute to the flux (201).

$$n\left(A(g)\right)_{source} = n\left(A(s)\right)_{sink} + n\left(A(g)\right)_{sink} \tag{201}$$

The **stationarity relation** $\varepsilon$ (202) is linking the fluxes $J(B)$ and $J(A)$ of the individual components of the system assuming that the net flux of the transport agent $X$ will vanish; $J(X) = 0$ [18].

$$\left( \frac{p^*(B) - x_{sink} \cdot p^*(A)}{p^*(X)} \right)_{T_{source}} = \left( \frac{p^*(B) - x_{sink} \cdot p^*(A)}{p^*(X)} \right)_{T_{sink}} = \varepsilon \tag{202}$$

The statement of the stationarity relation becomes applicable for the description of a chemical vapor transport by equation (203).

$$\frac{\left( \frac{p^*(B)}{p^*(X)} \right)_{T_{source}} - \left( \frac{p^*(B)}{p^*(X)} \right)_{T_{sink}}}{\left( \frac{p^*(A)}{p^*(X)} \right)_{T_{source}} - \left( \frac{p^*(A)}{p^*(X)} \right)_{T_{sink}}} = \frac{\Delta\lambda(B)}{\Delta\lambda(A)} = x_{sink} \tag{203}$$

Consequently, the fluxes $J(A)$ and $J(B)$ are proportional to the differences of the corresponding balance pressures in source and sink, normalized by the balance pressures for the solvent. In the same way the ratio $J(B) : J(A)$ is equal to the ratio of differences of the components gas phase solubilities [18]. Based on the extended transport model, this approach to the theoretical treatment of chemical vapor transport reactions is realized in the software package TRAGMIN [23]. In addition to calculation of equilibrium partial pressures and condensed phases the extended transport model offers further information on experimental realization and theoretical understanding of transport reactions [2]:

• Calculation of the transport efficiency of gas species and deduction of the prevailing transport reaction(s)

• Calculation of the influence of experimental conditions on the deposition of solids with homogeneity range, see $FeS_x$ [18-20].

• Calculation of the influence of experimental conditions on the deposition of multi-phasic solids, see $V_nO_{2n-1}$ [125 - 127].

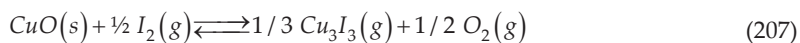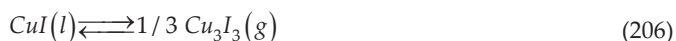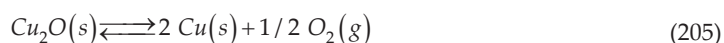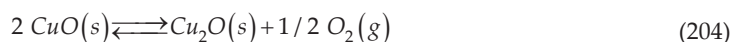### 4.3. Non–stationary transports (Co–operative transport model)

Using rather large amounts of a solid as source material together with sufficiently short experiment duration will yield quasi-stationary transport behavior (composition almost independent on time). Thus, deposition of a single phase solid of constant composition will be

possible. Non-stationary behavior occurs, if sequential migration of several different solids to the sink will be observed. The vapor transport of solids with homogeneity range, too, might be accompanied by a variation of the composition of the sink solid over time. Experimental evidence for *non-stationary* transport behavior can be obtained from series of transport experiments allowing for variable duration of the experiments. Much easier experimental access to non-stationary transport behavior is possible by using the so-called transport balance (see section 5). Despite charging a single-phase solid into a transport ampoule, a multi-phase equilibrium solid might form at the source region, due to the setting of chemical equilibrium at the beginning of the experiment [2, 139, 184 – 187]. Formation of *multi-phase* equilibrium solids at the source region of a transport ampoule can result from three reasons.

- Reaction between starting material and transport agent.

- Thermal decomposition of the starting material at the conditions of the transport experiment.

- Reaction between the starting material and the ampoule material (possibly involving the transport agent).

The observations made for the transport of copper(II) oxide by iodine [2, 185] can serve as an example for the complex phase relations and deposition sequences in chemical vapor transports. The transport behavior is characterized by partial thermal decomposition (204, 205) and the formation of condensed metal halides (206) occurring besides the actual transport reaction (207). Directed and reproducible syntheses depend not only on the appropriate molar ratios for the various components (copper, oxygen, iodine). The absolute amounts of starting materials and the ampoule volume are decisive too – since all components are solved at a substantial, however not equal, amount in the gas phase. The presence of multi-phase solids at the source at the beginning of the transport experiment leads to sequential migration of copper(II) oxide and copper(I) oxide, Figure 35.

$$2\ CuO(s) \rightleftharpoons Cu_2O(s) + 1/2\ O_2(g) \tag{204}$$

$$Cu_2O(s) \rightleftharpoons 2\ Cu(s) + 1/2\ O_2(g) \tag{205}$$

$$CuI(l) \rightleftharpoons 1/3\ Cu_3I_3(g) \tag{206}$$

$$CuO(s) + \tfrac{1}{2}\ I_2(g) \rightleftharpoons 1/3\ Cu_3I_3(g) + 1/2\ O_2(g) \tag{207}$$

Subsequent to initial equilibration the source solid consists of CuO and $Cu_2O$, the gas phase of $O_2$ (204, 205) and $Cu_3I_3$ (207). After transfer of the gas phase to the sink, cooling to the sink temperature leads to supersaturation of the gas phase, which eventually results in crystalli-
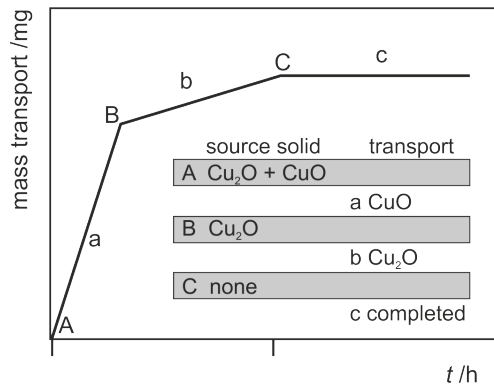
**Figure 35.** Non-stationary transport behavior of the CuO/I$_2$ system (1050 → 950 °C; 10 mg iodine), according to [185].

zation of the thermodynamically most stable phase, which is under the given conditions copper(II) oxide. Dissolution of copper(II) oxide at the source and its deposition at the sink result in the steady state (section a), which is characterized by constant ratio of fluxes from source to sink: $J(O)/J(Cu) = 1$ and $(1/2\ J(O_2))/(1/3\ (Cu_3I_3)) = 1$, respectively. After complete consumption of copper(II) oxide at the source, copper(I) oxide will be dissolved in a second steady state (section b). During the deposition of Cu$_2$O, the ratio of the fluxes are $J(O)/J(Cu) = 1/2$ and $(1/2\ J(O_2))/(1/3\ J(Cu_3I_3)) = 1/2$, since only O$_2$(g) and Cu$_3$I$_3$(g) are effective for the transport.

**The model of co-operating equilibrium zones ("model of co-operative transport")**. The calculation of the equilibrium solid(s) and gas phase in source and sink becomes possible applying the *model of co-operative transport* [22, 193]. It involves the minimization of the Gibbs energy according to Eriksson [188] for the two equilibrium regions of the transport ampoule. However, the main conceptual problem in modeling CVT experiments lies in the linking of the equilibrium calculations for the source and sink regions. In section 4.2 it has been described how the *extended transport model* can be applied to incongruent evaporation (and deposition) of solids in *quasi-stationary* transport experiments. In order to describe the complete (time dependent) transport behavior as a non *non-stationary* process, the model of co-operative transport uses an iterative calculation procedure [24].

For this purpose, the equilibrium condensed phase(s) of the source and sink obtained by a calculation cycle are kept at these regions. The source calculation of the subsequent cycle is performed without the molar amounts of the elements deposited at the sink in the preceding cycle. The stepwise ("cyclewise") transfer of the source solid(s) to the sink is simulated by repeated calculation cycles. The calculation is finished once no condensed phase is left at the source. Alternatively, the calculation is terminated when the source solid's composition remains stable from one cycle to the next – only the molar number of the solid is decreased. According to the stationarity criterion a steady state has been reached when the gas phase (in the source and sink) remains constant from one calculation cycle to the next. With respect to the mass transfer from the source to the sink, this means that within one calculation cycle the molar numbers of the source solid's components dissolved in the gas phase and deposited at

the sink are equal. If more than one condensed phase is involved in this process, we find simultaneous transport. This procedure gets by without explicit balancing of the fluxes of the individual gas species, in contrast to the flux relation [18 - 21].
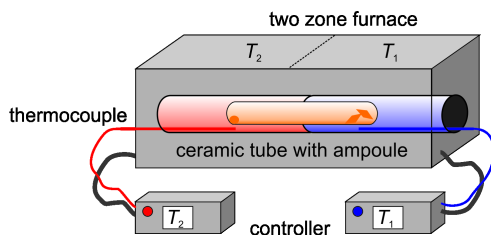
# 5. Experimental setup of CVT

Vapor transport experiments can be realized with different complexity. What kind of technique is used depends on the aim of the experiment. As shown in chapter 2.2, the setup as well as the specific parameters (substance amount of transport agent, temperature, temperature gradient) greatly influence the rate of mass transport. Accordingly, a high transport rate usually is chosen for the synthesis of a compound or the purification of it. If crystals are to be grown, the crystal quality is kept in mind and therefore rather smaller transport rates are aspired. In principle, two working methods can be applied for the practical realization in the laboratory: the transport in open or closed systems. In an open system a continuous flow of the transport agent is led over the source material; the solid, which is kept at a certain temperature, deposits at a different place with another temperature under the release of the transport agent. Transport reactions in an open system are often used for substance separation and purification. Due to the loss of the transport agent in the continuous gas flow only time-limited experiments in the range of some hours are realizable. Of course, high transport rates are intended for these experiments. In a closed system, typically a sealed ampoule, the transport agent remains in the system and consistently re-enters the reaction. Thus investigation periods of some days are attainable.

In most cases, transport reactions are executed in tubes or ampoules (diameter 10 to 20 mm) of a suitable glass. Today silica glass is frequently used, which is stable up to 1100 °C and quite inert to corrosive fillings. It is important to note that water is released during the heating of silica glass (water content up to 50 ppm). In order to avoid this, careful baking out of the ampoule in vacuum is recommended. Containers made from ceramic materials or glassy carbon can be integrated in a silica ampoule when highly corrosive materials have to be transported.

Vapor transport reactions take place in a temperature gradient. In order to set up the gradient in a controlled manner, tube furnaces with at least two independent heating zones are used, Figure 36. The transport furnace should be in a horizontal position in order to keep convection as part of the gas motion as small as possible. However, if the aim of the transport is the preparation of large amounts of substance by an endothermic transport, the furnace can be tilted so that the sink side is higher than the source side. This increases the transport rate. These experiments, however, cannot be described by the thermodynamic models that are based on gas motion by diffusion. The so-called *short-distance transport*, which was described by Krämer, uses specifically a high convective contribution to the gas motion [189]. The transport takes place in a vertical direction, over a distance of approximately 3 cm only. The ampoule cross section in such experiments is particularly large, 30 cm$^2$, Figure 37. This way, CVT also succeeds in systems that otherwise have a low transport rate due to an unfavorable equilibrium position.

This variation of the standard experimental set up is particularly effective for endothermic transport reactions. In cases of exothermic transport reactions, the convective part is omitted and the transport rate is exclusively determined by diffusion.



**Figure 36.** Experimental set up for chemical vapor transport in a conventional two-zone furnace, according to [2].
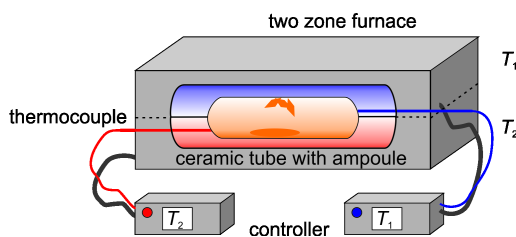


**Figure 37.** Experimental set up for chemical vapor transport in a short-distance two-zone furnace, according to [2, 189].

The experimental procedures for preparing transport ampoules can be different. Above all, they are dependent on the physical and chemical properties of the transport agent. First, the prepared ampoules are filled with approximately 0.5 up to 1 gram of the initial solid that is to be transported. For this purpose one uses a funnel long enough that the outlet is near the ampoule bottom. In the same way the transport agent can be added. Its amount is often selected so that the pressure (approximately expressed by the initial pressure of the transport agent) in the ampoule is 1 bar at the experiment temperature (calculated using the gas law). The transport ampoule and the vacuum line can be joined with a ground-glass joint. Alternatively, "quick-fit" joints have been established. Usually the contents of the ampoule must be cooled with liquid nitrogen before evacuation in order to avoid vaporization or sublimation of the respective transport agent. If iodine is used as transport agent, cooling is obligatory. If transport agents shall be used, which are already gaseous at room temperature (HCl, HBr, $Cl_2$, $Br_2$), more advanced techniques have to be applied for filling the ampoules [2]. These procedures can be avoided by using the ammonia halides as a source for the hydrogen halides and $PtCl_2$ or $CuCl_2$ for $Cl_2$. Finally, the reaction ampoule is evacuated and sealed under dynamic vacuum.

**Safety advice**: It is absolutely essential to avoid the condensation of liquid oxygen or moisture within the ampoule prior to sealing. If the ampoule is sealed in this state, a strong explosion

will be the result after the removal of the cooling agent due to very high pressure in the ampoule.

The prepared transport ampoule is placed in the middle of the furnace reaching both temperature zones. Before the actual transport experiments, usually a back transport or transport in a reverse temperature gradient is applied. This way, the ampoule walls on the sink side are freed of small crystallization seeds. Finishing the experiment the ampoule is taken out carefully. In order to obtain crystals without being contaminated by the condensed gas phase, one has to make sure that the gas phase condenses on the source side.
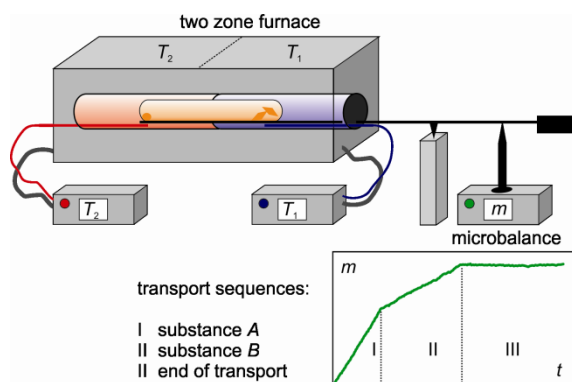


**Figure 38.** Determination of time dependent rates of mass transport using a transport balance, according to [2, 197].

For quite simple transport experiments, the determination of the transport rate is realized by weighing the crystals and calculation of an average rate within the total experimental time. More advanced, a transport balance can be applied, which is a measuring device for recording the time dependence of mass transports. In the process, the changes of the tracking force of the balance is recorded and graphically represented during the entire transport experiment. This way, the transport action can be followed online [133].

## Author details

Peer Schmidt[1], Michael Binnewies[2], Robert Glaum[3] and Marcus Schmidt[4]

1 Lausitz University of Applied Sciences, Faculty of Science, Senftenberg, Germany

2 Leibniz-University Hannover, Inorganic Chemistry, Hannover, Germany

3 University Bonn, Inorganic Chemistry, Bonn, Germany

4 Max-Planck-Institute of Chemical Physics of Solids, Dresden, Germany

# References

[1]  H. Schäfer, Chemische Transportreaktionen. Weinheim: Verlag Chemie; 1962.

[2]  M. Binnewies, R. Glaum, M. Schmidt, P. Schmidt, Chemical Vapor Transport Reactions. Berlin: De Gruyter; 2012.

[3]  F. Holleman, N. Wiberg, Lehrbuch der Anorganischen Chemie. Berlin: de Gruyter; 102. Edt. 2007.

[4]  R. Bunsen, J. Prakt. Chem. 1852; 56, 53.

[5]  E. van Arkel, J. H. de Boer, Z. Anorg. Allg. Chem. 1925; 148, 345.

[6]  E. van Arkel, Reine Metalle. Berlin: Springer; 1939.

[7]  R. Nitsche, Fortschr. Miner. 1967; 442, 231.

[8]  H. Schäfer, J. Cryst. Growth 1971; 9, 17.

[9]  E. Kaldis, Principles of the vapour growth of single crystals. In: C. H. L. Goodman (Ed.), Crystal Growth, Theory and Techniques. Vol. 1. 1974, 49.

[10]  J. Mercier, J. Cryst. Growth, 1982; 56, 235.

[11]  M. Lenz, R. Gruehn, Chem. Rev. 1997; 97, 2967.

[12]  M. Binnewies, Chemie in uns. Zeit 1998; 32, 15.

[13]  R. Gruehn, R. Glaum, Angew. Chemie 2000; 112, 706; Angew. Chem. Int. Ed. 2000; 39, 692.

[14]  K.-Th. Wilke, J. Bohm, Kristallzüchtung. Frankfurt: Harri Deutsch; 1988.

[15]  H. Schäfer, Z. Anorg. Allg. Chem. 1973; 400, 242.

[16]  M. Saeki, J. Crystal Growth 1976; 36, 77.

[17]  M. W. Richardson, B. I. Noläng, J. Crystal Growth 1977; 42, 90.

[18]  G. Krabbes, H. Oppermann, E. Wolf, Z. Anorg. Allg. Chem. 1975; 416, 65.

[19]  G. Krabbes, H. Oppermann, E. Wolf, Z. Anorg. Allg. Chem. 1976; 421, 111

[20]  G. Krabbes, H. Oppermann, E. Wolf,. Z. Anorg. Allg. Chem. 1976; 423, 212.

[21]  G. Krabbes, H. Oppermann, E. Wolf, J. Crystal Growth 1983; 64, 353.

[22]  R. Gruehn, H. J. Schweizer, Angew. Chem. 1983; 95, 80.

[23]  G. Krabbes, W. Bieger, K.-H. Sommer, T. Söhnel, U. Steiner, Computerprogramm TRAGMIN, Version 5.0, IFW Dresden, TU Dresden, HTW Dresden, 2008. http://www2.htw-dresden.de/~webchem/steiner/Tragmin/tragmin.htm

[24] O. Trappe, R. Glaum, R. Gruehn, Das Computerprogramm CVTRANS, Universität Gießen, 1999. http//www.glaum.chemie.uni-bonn.de/forschung/cvtrans

[25] H. Oppermann, M. Schmidt, P. Schmidt, Z. Anorg. Allg. Chem. 2005; 631, 197.

[26] S. Hampel, M. Ruck, P. Schmidt, Z. Anorg. Allg. Chem. 2005; 631, 272.

[27] K. H. Berthel, R. Hedderich, B. Pietraß, In: Proc. 5th Internat. Symp. High Purity Materials in Science and Techn., Dresden, 1980; R. Hedderich, PhD thesis. Academy of Sciences of GDR, Berlin; 1980; D. Rhede, PhD thesis, Academy of Sciences of GDR, Berlin, 1982.

[28] H. Oppermann, A. S. Okhotin, Adv. Space Res. 1981; 1, 51; H. Oppermann, In: Freiberger Forschungshefte, VEB Deutscher Verlag für Grundstoffindustrie 1987; A 767, 97.

[29] H. Schornstein, R. Gruehn, Z. Anorg. Allg. Chem. 1988; 561, 103.

[30] H. Schornstein, R. Gruehn, Z. Anorg. Allg. Chem. 1989; 579, 173.

[31] H. Oppermann, M. Ritschel, Kristall Techn. 1975; 10, 485.

[32] H. Oppermann, P. Schmidt, Z. Anorg. Allg. Chem. 2005; 631, 1309.

[33] M. Binnewies, Z. Anorg. Allg. Chem. 1977; 435, 156.

[34] H. Schäfer, Z. Anorg. Allg. Chem. 1974; 403, 116.

[35] H. Schäfer, J. Cryst. Growth, 1975; 31, 31.

[36] H. Schäfer, Angew. Chem. 1976; 88, 775; Angew. Chem., Int. Ed. 1976; 15, 713.

[37] H. Schäfer, Adv. Inorg. Radiochem. 1983; 26, 201.

[38] M. Binnewies, H. Schäfer, Z. Anorg. Allg. Chem. 1974; 407, 327.

[39] L. H. Ngai, F. E. Stafford, In: L. Eyring (Ed.) Advances in High Temperature Chemistry. New York, Academic Press, 1971, 313.

[40] H. Schäfer, In: Nat. Bur. Standards, Spec. Publ. 364, Solid State Chem. Proceed.5th Materials Research Sympos., 1972, 413.

[41] S. Lieke und M. Binnewies, Z. Anorg. Allg. Chem. 1997; 623, 1705.; M. Binnewies, K. Jug, Eur. J. Inorg. Chem. 2000; 1127.

[42] M. Binnewies, H. Schnöckel, Chem. Rev. 1990; 90, 32.

[43] H. Schäfer, F. Wehmeier, M. Trenkel, J. Less-Common Met. 1968; 16, 290.

[44] M. Binnewies, Z. Anorg. Allg. Chem. 1976; 422, 43.

[45] R. Köppe, J. Steiner, H. Schnöckel, Z. Anorg. Allg. Chem. 2003; 62, 2168.

[46]  R. Köppe, H. Schnöckel, Angew. Chem. 2004; 116, 2222; Angew. Chem., Int. Ed. 2004; 43, 2170.

[47]  K. A. Gingerich, E. Kaldis, Eds., Current Topics in Material Science, North-Holland Publishing Company, 1980; 6, 345.

[48]  H. Schäfer, Z. Anorg. Allg. Chem. 1986; 543, 217.

[49]  H. Schäfer, A. Tebben, Z. Anorg. Allg. Chem. 1960; 304, 317.

[50]  S. Tamaru, N. Ando, Z. Anorg. Allg. Chem. 1929; 184, 385; S. Tamaru, N. Ando, Z. Anorg. Allg. Chem. 1931; 195, 309.

[51]  K. Matsumoto, S. Kaneko, K. Katagi, J. Cryst. Growth. 1977; 40, 291.

[52]  J. M. Brom, W. Weltner, J. Mol. Spectrosc. 1973; 45, 82.

[53]  M. Binnewies, Z. Anorg. Allg. Chem. 1990; 589, 115.

[54]  K. C. Mills, Thermodynamic Data for Inorganic Sulfides, Selenides and Tellurides. London; Butterworths, 1974.

[55]  K. Dressler, Helv. Phys. Acta. 1955; 28, 563.

[56]  H. Schäfer, W. Beckmann, Z. Anorg. Allg. Chem. 1966; 347, 225.

[57]  G. Krabbes, H. Oppermann, Z. Anorg. Allg. Chem. 1981; 481, 13.

[58]  D. Britnell, G. W. A. Fowles, R. Mandycewsky, Chem. Commun. 1970; 608.

[59]  E. Milke, R. Köppe, M. Binnewies, Z. Anorg. Allg. Chem. 2010; 636, 1313.

[60]  H. Oppermann, M. Schmidt, H. Brückner, W. Schnelle, E. Gmelin, Z. Anorg. Allg. Chem. 2000; 626, 937.

[61]  H. Schäfer, U. Wiese, J. Less-Common Met. 1971;, 24, 55.

[62]  K. L. Choy, Progress in Materials Science 2003; 48, 57.

[63]  R. F. Rolsten, Z. Anorg. Allg. Chem. 1960; 305, 25.

[64]  R. F. Rolsten, Iodide Metals and MetaI Iodides. New York, J. Wiley, 1961.

[65]  H. Schäfer, M. Trenkel, Z. Anorg. Allg. Chem. 1975; 414, 137.

[66]  L. Mond, C. Langer, F. Quincke, J. Chem. Soc. 1890; 749.

[67]  E. van Arkel, Physica 1923; 3, 76.

[68]  E. van Arkel, Metallwirtschaft 1934; 13, 405.

[69]  J. H. de Boer, J. D. Fast, Z. Anorg. Allg. Chem. 1926; 153, 1.

[70]  J. H. de Boer, J. D. Fast, Z. Anorg. Allg. Chem. 1930; 187, 193.

[71]  R. A. J. Shelton, Trans. Faraday Soc. 1966; 62, 222.

[72]  T. Hashino, T. Kawai, Trans. Faraday Soc. 1967; 63, 3088.

[73]  J. Cueilleron, J. C. Viala, J. Less-Common Met. 1978; 58, 123.

[74]  H. C. Spirlet, J. Phys. Colloq. 1979; 40, 87.

[75]  D. M. Speros, R. M. Caldwell, W. E. Smyser, High Temp. Sci. 1972; 4, 99.

[76]  H. Schäfer, M. Trenkel, Z. Anorg. Allg. Chem. 1979; 458, 234.

[77]  M. Kotrbová, Z. Hauptman, Krist. Tech. 1967; 2, 505.

[78]  J. H. Dettingmeijer, B. Meinders, L. M. Nijland, J. Less-Common Met. 1974; 35, 159.

[79]  H. Schäfer, T. Grofe, M. Trenkel, J. Sol. State. Chem. 1973; 8, 14.

[80]  H. Schäfer, A. Tebben, W. Gerhardt, Z. Anorg. Allg. Chem. 1963; 321, 41.

[81]  H. Schäfer, W. Gerhardt, Z. Anorg. Allg. Chem. 1984; 512, 79.

[82]  L. Hannevold, O. Nilsen, A. Kjekshus, H. Fjellvåg, J. Cryst. Growth 2005; 279, 206.

[83]  R. Loitzl, C. Schüler, German Patent DE 2051404, 1972.

[84]  M. Richardson, Acta Chem. Scand. 1967; 21, 2305.

[85]  O. Bosholm, H. Oppermann, S. Däbritz, Z. Naturforsch. 2001; 56b, 329.

[86]  H. Wilhelm, M. Schmidt, R. Cardoso-Gil, U. Burkhardt, M. Hanfland, U. Schwarz, L. Akselrud, Science Technol. Adv. Mater. 2007; 8, 416.

[87]  O. Bosholm, H. Oppermann, S. Däbritz, Z. Naturforsch. 2000; 55b, 614.

[88]  O. Bosholm, H. Oppermann, S. Däbritz, Z. Naturforsch. 2000; 55b, 1199.

[89]  R. Krausze, M. Khristov, P. Peshev, G. Krabbes, Z. Anorg. Allg. Chem. 1989;579, 231.

[90]  R. Krausze, M. Khristov, P. Peshev, G. Krabbes, Z. Anorg. Allg. Chem. 1990; 588, 123.

[91]  R. Neddermann, S. Gerighausen, M. Binnewies, Z. Anorg. Allg. Chem. 1996;622, 21.

[92]  H. Schäfer, J. Nowitzki, Z. Anorg. Allg. Chem. 1977; 435, 49.

[93]  J. J. Nickl, J. D. Koukoussas, A. Mühlratzer, J. Less-Common Met. 1973; 32, 243.

[94]  T. Plaggenborg, M. Binnewies, Z. Anorg. Allg. Chem. 2000; 626, 1478.

[95]  H. Oppermann, Solid State Ionics 1990; 39, 17.

[96]  K. Brodersen, H. K. Breitbach, G. Thiele, Z. Anorg. Allg. Chem. 1968; 357, 162.

[97]  R. E. Mc Carley, J. W. Roddy, K. O. Berry, Inorg. Chem. 1964; 3, 50.

[98]  H. Schäfer, Angew. Chem. 1976, 88; 775, Angew. Chem. Int. Ed. 1976; 15, 713.

[99]  H. Schäfer, Adv. Inorg. Nucl. Chem. 1983; 26, 201.

[100] H. Schäfer, J. Cryst. Growth 1975; 31, 31.

[101] H. Schäfer, Z. Anorg. Allg. Chem. 1980; 469, 123.

[102] R. Krausze, H. Oppermann, Z. Anorg. Allg. Chem. 1987; 550, 123.

[103] H. A. Oye, D. M. Gruen, J. Amer. Chem. Soc. 1969; 91, 2229.

[104] D. M. Gruen, H. A. Oye, Inorg. Nucl. Chem. Lett. 1967; 3, 453.

[105] K. Lascelles, H. Schäfer, Z. Anorg. Allg. Chem. 1971; 382, 249.

[106] H. Schäfer, M. Binnewies, W. Domke, J. Karbinski, Z. Anorg. Allg. Chem. 1974; 403, 116.

[107] H. Gunsilius, W. Urland, R. Kremer, Z. Anorg. Allg. Chem. 1987; 550, 35.

[108] K. Shinozaki, Y. Hirashima, G. Adachi, Trans. Nonferrous Met. Soc. China 1990; 16, 42.

[109] G.-Y. Adachi, K. Shinozaki, Y. Hirashima, K.-I. Machida, J. Less-Common Met. 1991; 169,

[110] K. Murase, K. Shinozaki, K.-I. Machida, G.-Y. Adachi, Bull. Chem. Soc. Jpn. 1992; 65, 2724.

[111] K. Murase, K. Shinozaki, Y. Hirashima, K.-I. Machida, G.-Y. Adachi, J. Alloys Compd. 1993; 198, 31.

[112] J. Yu, Y. Yu, Z. Wang, Jinshu Xuebao (Acta Metallurgica Sinica) 1997; 3, 391.

[113] T. Ozaki, K.-I. Machida, G.-Y. Adachi, Rare Earths 1998; 32, 154.

[114] T. Ozaki, J. Jiang, K. Murase, K.-I. Machida, G.-Y. Adachi, J. Alloys Compd. 1998; 265, 125.

[115] T. Ozaki, K.-I. Machida, G.-Y. Adachi, Metall. Mater. Trans. 1999; 30 B, 45.

[116] Z.-C. Wang, Y.-H. Sun, L. Guo, J. Alloys Compd. 1999; 287, 109.

[117] Y. H. Wang, L. S. Wang, J. Chinese Rare Earth Soc. 2000; 18, 74.

[118] D. Yang, J. Yu, J. Jiang, Z. Wang, J. Mater. and Metall. 2003; 2, 113.

[119] Bonnamy, J. C. Launay, M. Pouchard, Rev. Chim. Min. 1978; 15, 178.

[120] W. Redlich, T. Petzel, Rev. Chim. Min. 1983; 20, 54.

[121] L.-P. Zenser, Dissertation, University of Gießen, 1999.

[122] J. Mercier, G. Fourcaudot, Y. Monteil, C. Bec, R. Hillel, J. Cryst. Growth 1982; 59, 599.

[123] W. Reichelt, PhD thesis. Academy of Sciences of GDR, Berlin; 1977.

[124] Rossberg, H. Oppermann, Z. Anorg. Allg. Chem. 1988; 556, 109.

[125]  H. Oppermann, W. Reichelt, G. Krabbes, E. Wolf, Krist. Tech. 1977; 12, 717.

[126]  H. Oppermann, W. Reichelt, G. Krabbes, E. Wolf, Krist. Tech. 1977; 12, 919.

[127]  H. Oppermann, W. Reichelt, E. Wolf, Z. Anorg. Allg. Chem. 1977; 432, 26.

[128]  H. Schäfer, M. Binnewies, H. Rabeneck, C. Brendel, M. Trenkel, Z. Anorg. Allg. Chem. 1977; 435, 5.

[129]  H. Oppermann, V. A. Titov, G. Kunze, G. A. Kokovin, E. Wolf, Z. Anorg. Allg. Chem. 1978; 439, 13.

[130]  H. Oppermann, G. Kunze, E. Wolf, G. A. Kokovin, I. M. Sitschova, G. E. Osigova, Z. Anorg. Allg. Chem. 1980; 461, 165.

[131]  M. Spieß, R. Gruehn, Naturwissenschaften 1978; 65, 594.

[132]  L. Bald, R. Gruehn, Z. Anorg. Allg. Chem. 1984; 509, 23.

[133]  V. Plies, T. Kohlmann, R. Gruehn, Z. Anorg. Allg. Chem. 1989; 568, 62.

[134]  T. Dahmen, R. Gruehn, Z. Anorg. Allg. Chem. 1995; 621, 417.

[135]  M. S. Islam, R. Glaum, Z. Anorg. Allg. Chem. 2009; 635, 1008.

[136]  R. Glaum, M. Weil, D. Özalp, Z. Anorg. Allg. Chem. 1996; 622, 1839.

[137]  Kostencki, PhD thesis, University of Gießen; 1997.

[138]  R. Glaum, Neue Untersuchungen an wasserfreien Phosphaten der Übergangsmetalle, Habilitation, University of Gießen; URL: http://www.geb.uni-giessen.de.

[139]  Litterscheid, Diploma thesis, University of Bonn; 2003.

[140]  M. Weil, Z. Naturforsch. 2000; 55b, 699; M. Weil, Acta Crystallogr. 2001; E57, i22; M. Weil, Acta Crystallogr. 2001; E57, i28; M. Weil, C. Lengauer, E. Fueglein, E. J. Baran, Cryst. Growth Des. 2004; 4, 1229; M. Weil, Z. Anorg. Allg. Chem. 2004; 630, 213; M. Weil, Acta Crystallogr. 2004; E60, i139; M. Weil, U. Kolitsch, Z. Kristallogr. 2005; 22 Suppl., 183.

[141]  M. A. Daubrée, Ann. Mines 1841; 20, 65. Cited in: W. Schrön, Eur. J. Mineral. 1989; 1, 739. M. A. Daubrée, Compt. Rend. 1849; 29, 227. Cited in: W. Schrön, Eur. J. Mineral. 1989; 1, 739.

[142]  Kaldis, R. Verreault, J. Less-Common Met. 1970; 20, 177; E. Kaldis, J. Cryst. Growth, 1971; 9, 281.

[143]  R. Schober, E. Thilo, Chem. Ber. 1940; 73, 1219.

[144]  R. Diehl, A. Räuber, F. Friedrich, J. Cryst. Growth 1975; 29, 225.

[145]  H. Schmid, J. Phys. Chem. Solids 1965; 27, 973.

[146]  K. Nassau, J. W. Shiever, J. Cryst. Growth 1972; 16, 59.

[147] G. Castellanos-Guzman, M. Trujillo-Torrez, M. Czank, Mater. Science Engin. 2005; B 120, 59.

[148] J. Campa-Molina, S. Ulloa-Godınez, A. Barrera, L. Bucio, J. Mata, J. Phys.: Condens. Matter 2006; 18, 4827

[149] T. Takahashi, O. Yamada, J. Cryst. Growth 1976; 33, 361.

[150] R. Nitsche, J. Phys. Chem. Solids 1960, 17, 163. R. Nitsche, H. U. Bölsterli, M. Lichtensteiger, J. Phys. Chem. Solids 1961; 21, 199.

[151] Menzel, R. Kaden, D. Spemann, K. Bente, T. Butz, Nucl. Instr. Meth. Phys. Res. B 2006; 249, 478.

[152] Wolf, H. Oppermann, G. Krabbes, W. Reichelt, Current Topics in Materials Science 1978; 1, 697.

[153] Krabbes, H. Oppermann, Z. Anorg. Allg. Chem. 1979; 450, 27.

[154] R. Nitsche, J. Phys. Chem. Solids, Suppl. 1967; 1, 215.

[155] P. B. Rimmington, A. Balchin, B. K. Tanner, J. Cryst. Growth 1972; 21, 171.

[156] U. Hotje, R. Wartchow, M. Binnewies, Z. Anorg. Allg. Chem. 2005; 631, 403.

[157] K. Kimoto, K. Masumoto, Y. Noda, K. Kumazawa, T. Kiyosawa, N. Koguchi, Jpn. J. Appl. Phys., Part 1, 1993, 32 (Suppl. 32−3, Proceedings of the 9th International Conference of Ternary and Multinary Compounds, 1993; 187.

[158] E. Catano, Z. K. Kun, J. Cryst. Growth 1976; 33, 324.

[159] U. Hotje, C. Rose, M. Binnewies, Z. Anorg. Allg. Chem. 2005; 631, 2501.

[160] B. Van den Berg, J. E. van Delden, J. Boumann, Phys. Status Solidi 1969; 36, K 89.

[161] P. Gibart, A. Begouen-Demeaux, Compt. Rend. Acad. Sci. Paris C 1969; 268, 111.

[162] Hartmann, R. Mach, N. Testova, J. Cryst. Growth 1987; 84, 199.

[163] Matsumoto, Shizuoka Daigaku Denshi Kogaku Kenkyusho Kenkyu Hokoku 1988; 23, 127.

[164] Ito, Y. Matsuura, Proc. Electrochem. Soc. 1979; 79, 281.

[165] G. Attolini, C. Paorici, L. Zanotti. J. Cryst. Growth 1982; 56, 254.

[166] G. Attolini, C. Paorici, Mater. Chem. Phys. 1983; 9, 65.

[167] S. Locmelis, U. Hotje, M. Binnewies, Z. Anorg. Allg. Chem. 2005; 631, 672.

[168] H. Schäfer, Z. Anorg. Allg. Chem. 1982; 486, 33.

[169] W. Kleber, I. Mietz, U. Elsasser, Kristall Technik 1967; 2, 327.

[170] A.G. Sigai, H. Wiedemeier, J. Electrochem. Soc. 1972; 119, 910.

[171] Y. G. Sha, C. H. Su, W. Palosz, M P. Volz, D. C. Gillies, F. R. Szofran, S. L. Lehoczky, H. C. Liu, R. F. Brebrick, J. Cryst. Growth 1995; 146, 42.

[172] Paorici, Proc. Int. Symp. Cadmium Telluride, Mater. Gamma-Ray Detectors 1972; VII-1–VII-4.

[173] Y. G. Akhromenko, G. A. Il'chuk, I. E. Lopatinskii, S. P. Pavlishin, Izv. Akad. Nauk SSSR, Neorg. Mater. 1981; 17, 2016.

[174] V. V. Tokmakov, I. I. Krotov, A. V. Vanyukov, Izv. Akad. Nauk SSSR, Neorg. Mater. 1979; 15, 1546.

[175] Munster, G. Rinck, W. Ruppert, Z. Phys. Chem. 1956; 9, 228.

[176] Ruck, Z. Anorg. Allg. Chem. 1999;, 625, 2050.

[177] J. Martin, R. Gruehn, Z. Kristallogr. 1988; 182, 180.

[178] Özalp, PhD thesis, University of Gießen; 1992.

[179] Lenz, PhD thesis, University of Gießen; 1995

[180] R. Köppe, H. Schnöckel, Z. Anorg. Allg. Chem. 2003; 629, 2168.

[181] P. Bolte, R. Gruehn, Z. Anorg. Allg. Chem. 1994; 620, 2077.

[182] C. N. Cochran, L. M. Foster, J. Electrochem. Soc., 1962; 109, 144.

[183] C. J. Frosch, J. Electrochem. Soc. 1964; 111, 180.

[184] K. Nocker, R. Gruehn, Z. Anorg. Allg. Chem. 1993; 619, 699; K. Nocker, PhD thesis, University of Gießen; 1993.

[185] Trappe, Diploma thesis, University of Gießen; 1994

[186] J. Seiwert, R. Gruehn, Z. Anorg. Allg. Chem. 1984; 510, 93.

[187] H.-J. Schweizer, PhD thesis, University of Gießen; 1983.

[188] Eriksson, Acta Chem. Scand. 1971; 25, 2651.

[189] V. Krämer, R. Nitsche, M. Schumacher J. Cryst. Growth 1974; 24.25, 179.