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Developments in Measuring and Calculating Chemical Vapor Transport Phenomena Demonstrated on Cr, Mo, W, and Their Compounds

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Contents

I. Introduction

To a solid-state chemist heterogeneous reactions between a condensed phase and a reactive gas phase—acting as a solvent—offer numerous and varied aspects of interesting observations. If an otherwise nonvolatile solid migrates in a temperature gradient, crystals may grow and only then their crystallographic and physical properties become accessable. Thus formed compounds may be metastable and not be obtainable in any other way at all. Important information on the transport behavior can be obtained by measuring the mass flux and the amount of the deposited solids, respectively, and comparing them with thermodynamic models. In this way, extensive calculations stimulated the development of the halogen lightbulb. These developments—important for the application—will be

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referred to but will not be discussed. The involvement of a hitherto unknown gaseous species may be indicated by the experimental data that do not agree with model calculations at all.

We will report new possibilities of measuring the mass flux inside a closed ampule. The correlation of thermochemical calculations with experimental data is particularly proven in the systems containing Cr, Mo, W, or their compounds.

II. Transport Experiments

A. General

The transport experiments are mostly carried out in closed silica tubes having an inner diameter of about 10−20 mm and a length of about 10−20 cm (for general aspects see Schäfer[1]). Prior to loading, the tubes are usually cleaned and degassed under reduced pressure of 10^{-5} atm or less and at temperatures about 1000 °C, thus reducing the water content.[2,3] The samples are introduced into the ampule, and the transport agent is added. After the tube is evacuated, it is sealed off at different pressures, depending on the kind of transport agent. The loaded tube is placed in a temperature gradient (two- or three-zone tubular furnace with thermocouples). The furnace can be fixed in horizontal or vertical position.

B. Determination of the Transport Rates

After an experiment is terminated, the transport rate can be determined from the weight of the deposited solid recovered and the total time elapsed, provided that the transport rate was constant during the experiment (“steady-state behavior”) and that solids were present in both source and sink.

The transport rate can be measured for various transport agent concentrations (cf., Figure 1), temperatures (mean temperature $\bar{T} = {}^1/_2(T_2 + T_1)$ or difference of temperatures $\Delta T = |T_2 - T_1|$ of sink and source (cf., Figure 2, section III.B.1)), dimensions of

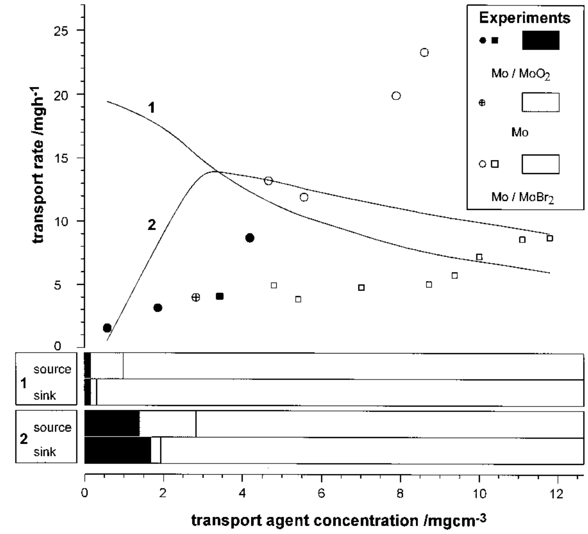

Figure 1. Experimental and calculated transport rates $\dot{m}$(Mo) and equilibrium solids at sink and source (1000 → 900 °C) in the system Mo/H_2O/$HgBr_2$ depending on transport agent concentration $c(HgBr_2)$. Curve 1 is calculated with $c(H_2O) = 2.5 \times 10^{-3}$ mmol/cm^3. Curve 2 with $c(H_2O) = 2.5 \times 10^{-4}$ mmol/cm^3 (both $D_o = 0.1$ cm^2/s). Experiments with two different cross sections of the ampule $q = 2$ cm^2 (●) and $q = 0.95$ cm^2 (■).[10]

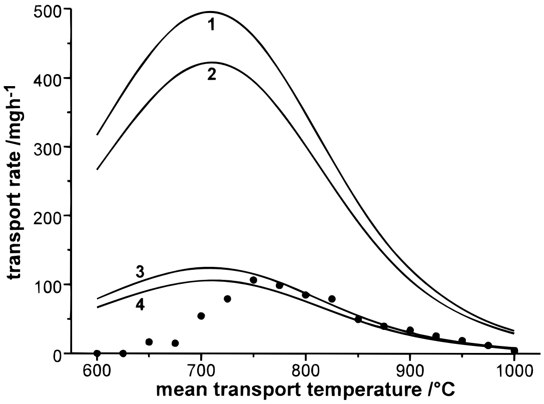

Figure 2. Experimental and calculated transport rates $\dot{m}(WO_2)$ in the system WO_2/H_2O/$HgBr_2$ depending on the mean transport temperature $\bar{T}$ ($\Delta T = 100$ °C; $c(HgBr_2) = 3.60$ mg/cm^3). Curve 1 is calculated with $c(H_2O) = 2.5 \times 10^{-3}$ mmol/cm^3, curve 2, with $c(H_2O) = 2.5 \times 10^{-4}$ mmol/cm^3 (both $D_o = 0.1$ cm^2/s); curve 3, with $c(H_2O) = 2.5 \times 10^{-3}$ mmol/cm^3; curve 4, with $c(H_2O) = 2.5 \times 10^{-4}$ mmol/cm^3 (both $D_o = 0.025$ cm^2/s). The experimental values (●) were standardized to a diffusion length of 10 cm and a cross section of 2.0 cm^2 of the ampules.[14]

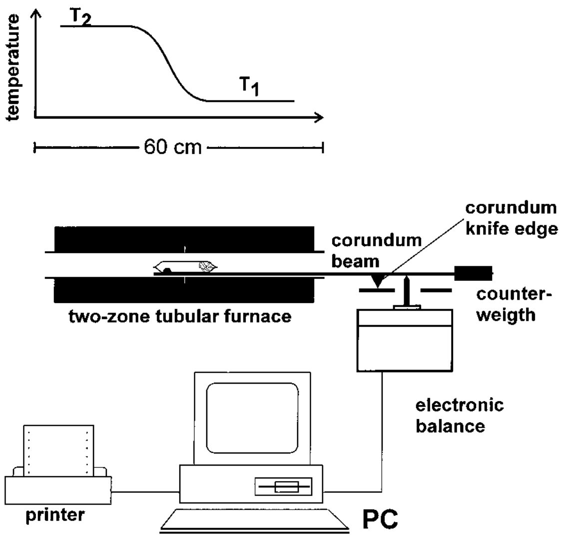

Figure 3. Schematic presentation of the transport balance (from Plies *et al.*[9]).

the tube (cross section or length), or orientation of the tube with respect to the gravity vector.

In the past several attempts were made to measure the rate of material transport in real time during vapor phase crystal growth in closed silica ampules: Geary and Hough,[4] Jeffes and Marples,[5] Olson,[6] Wiedemeier and Chandra,[7] Olson and Powell,[8] and Plies *et al.*[9] In all cases the ampule was connected to a mass balance displaying changes of mass within the ampule. The ampule can be connected to the balance in different ways: (1) the ampule lies on a horizontal support, the ends of which are attached to the ends of the extended balance arm;[4] (2) the ampule lies on a horizontal support and one end of the beam is attached to the balance (cf., Figure 3);[9] (3) an extension of the ampule is connected to the balance;[5,6] (4) the ampule is supported by a fulcrum close to the source end while the other end is connected, via an extension rod, to the hang-down wire of a vacuum balance;[7] or (5) the ampule is attached to the balance via silica fibers, which pass through holes in the furnace wall.[8]

By using the technique ("transport balance") of Plies *et al.*[9] it became possible to detect and determine (i) several consecutive steady states (e.g., in the systems Mo/$MoBr_2$/$HgBr_2$/H_2O[10] and W/WO_2/$HgBr_2$/H_2O[11]); (ii) nonstationary transport effects (CoP/CoI_2/I_2/H_2,[12] GeO_2/WO_2/H_2O,[9] CrOCl/Cr_2O_3/Cl_2/H_2O,[13] and $NiSO_4$/$PbSO_4$/$PbCl_2$[9]); (iii) kinetic effects (W/WO_2/$HgBr_2$[11] and WO_2/$HgBr_2$[14]); and (iv) the loss of mass of a solid due to dissolution in the gas phase (Rh_2O_3/Cl_2[15] and WO_2/$HgBr_2$[14]).

The different effects (i–iv) on the mass/time diagrams are demonstrated in Figure 4.

For open systems another technique of studying heterogeneous reactions (gas–solid) at high temperatures was reported by Factor and Garrett.[16]

Schönherr and Wojnowski presented a computer-assisted video technique to continously determine the contour of the deposition in a closed ampule.[17] A similar technique is reported by Negishi *et al.*[18]

III. Theoretical Treatment of the Chemical Transport Process

A. General Aspects

The migration of a condensed phase in a temperature gradient can be caused by several processes: (i) sublimation without decomposition, (ii) catalytic sublimation,[3,19–22] (iii) dissociative sublimation,[23–27] (iv) distillation, and (v) chemical transport. While sublimation and distillation reactions lead to the migration of the substance to the lower temperature of a temperature gradient, the direction of chemical transport reactions depends on the sign of heat of reaction $\Delta_R H°$.

General aspects of the crystal growth from the gas phase are discussed in the monographs by Schäfer,[1] Factor and Garrett,[28] and Wilke and Bohm[29] and the paper of Nitsche.[30]

For a crystal grower the following aspects are of general interest: (1) morphology and perfection of the crystals, (2) transport rates of the deposited phases, and (3) equilibrium composition of the condensed phase (and the gas phase). The a priori calculation of the equilibria and of the rates of deposition are the subject of the following chapters.

B. Calculation of the Equilibrium

1. General Aspects

Exothermic reactions ($\Delta_R H°_T < 0$) cause migration into the region of higher temperature ($T_1 \rightarrow T_2$, $T_1 < T_2$) and endothermic reactions ($\Delta_R H°_T > 0$) into the opposite direction (cf., Figure 5—transport of SiAs by means of I_2[31]). Exothermic reactions lead to positive slopes in the log K_P vs $1/T$ diagrams (eq III.1), while endothermic reactions result in negative ones (for details see, i.e., Jeffes,[32] Wehmeier,[33] Schäfer,[34] and Oppermann[35]).

The equilibrium state of a system can be described by the following relation:

$$\Delta_R G°_T = \Delta_R H°_T - T\,\Delta_R S°_T = -RT \ln K_{P,T} \qquad \text{(III.1)}$$

where $\Delta_R G°_T$ stands for standard free energy of reaction at temperature T; $\Delta_R H°_T$, standard enthalpy of reaction at temperature T; $\Delta_R S°_T$, standard entropy of reaction at temperature T; $K_{P,T}$, equilibrium constant at temperature T; R, universal gas constant; and T, temperature.

According to Chandra and Wiedemeier[36] three procedures can be used to calculate equilibrium conditions (e.g., partial pressures, mole fractions, etc.):

a. Independent Isothermal Zone Method. The equilibrium pressures are independently calculated for the sink and source region. A model ampule is positioned in a temperature gradient $T_2 \rightarrow T_1$ and is hypothetically divided into two zones (regions), one belonging to the lower temperature T_1 and the other one having the higher temperature T_2. Equal amounts of transport agent are attributed to each zone. The isothermal calculations for the two zones are not linked (e.g., by a mass balance) and the total pressures obtained are different for the two regions.

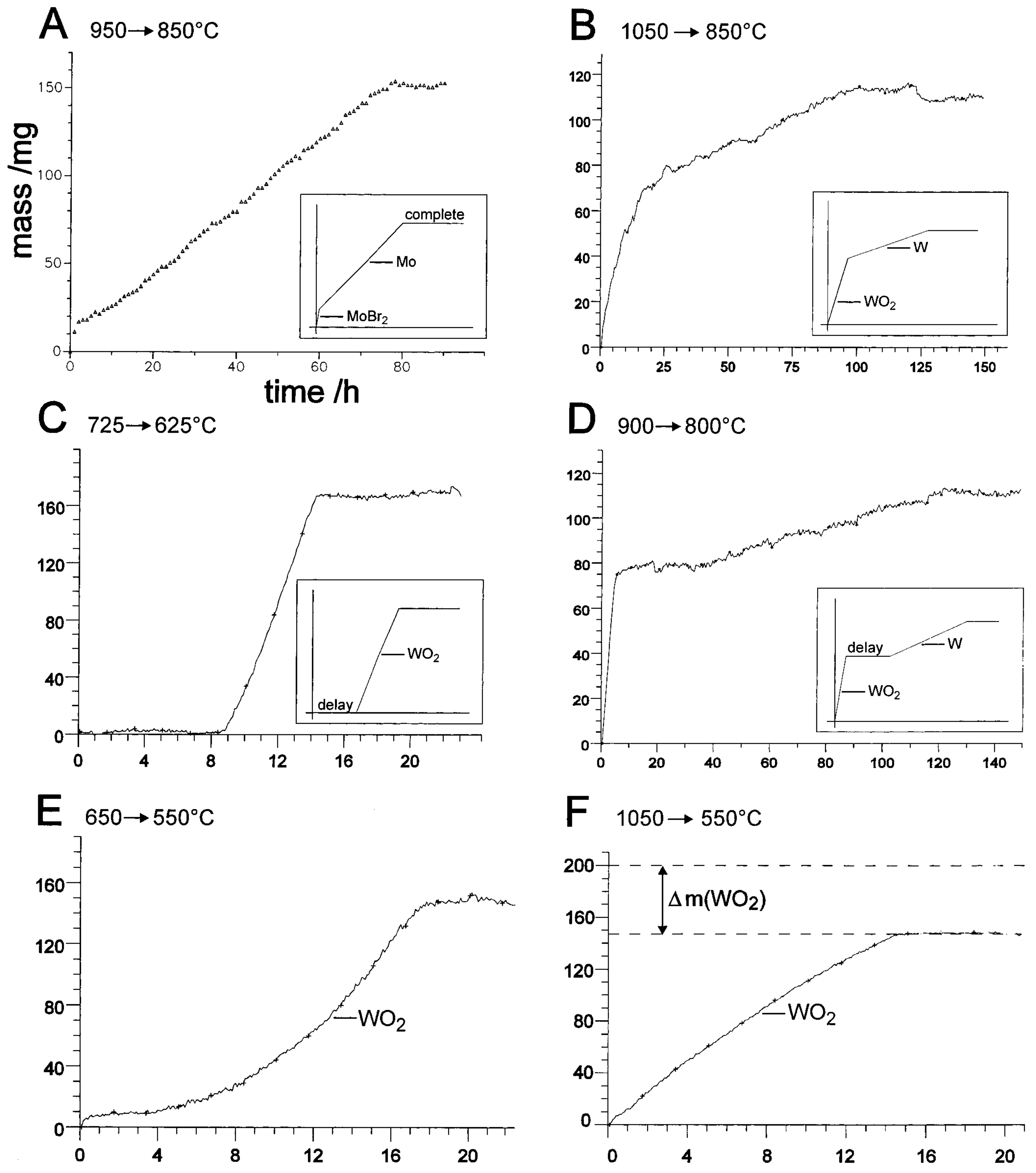

Figure 4. Mass/time diagrams measured by the technique of Plies *et al.* (transport balance)[9] and idealized diagrams (in box): Mass rate A, of $MoBr_2$ (first steady state) and Mo (second steady state);[10] B, of WO_2 (first steady state) and W (second steady state);[11] C, of WO_2 (with kinetic hinderance of deposition);[14] D, of WO_2 (first steady state) and W (second steady state, kinetic hinderance of deposition);[11] E, of WO_2 (nonstationary transport);[14] F, of WO_2 (starting amount 200 mg, mass loss of WO_2),[14] in all cases $HgBr_2$ as transport agent ($c(HgBr_2) = 3.60$ mg/cm^3).

b. Coupled Isothermal Zone Method. Calculations are carried out under the condition that the total pressures in the two (or more) hypothetical isothermal zones are equal, which is realized by adding different amounts of transport agent to the different zones.

c. Representative Isothermal Zone Method. In a first step the transport ampule is assumed to be not in a distinct temperature gradient and to be not hypothetically partitioned. The total pressure solely depends on the amount of added transport agent and the mean transport temperature.

Then the ampule is hypothetically partitioned into two zones, and by keeping the just-determined total pressure, the partial pressures are calculated by using method b and applying a temperature gradient.

In practice the differences in partial pressures give rise to a mass flux between the two temperature

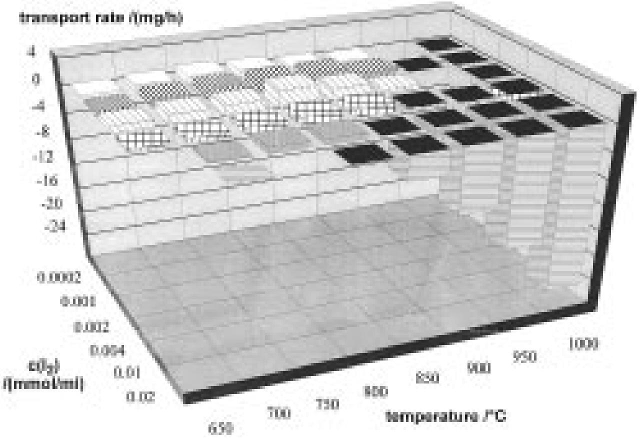

Figure 5. Experimental transport rates $\dot{m}$(SiAs) in the system SiAs/I.[31] $\dot{m}_{exp} < 0$ means endothermic transport processes and are marked by black tops of the bars. Experiments with similar transport agent concentration are marked by identical hatching. Missing bars indicate no transport effect.

regions. Model a is a rather crude one, while model c comes much closer to the truly existing conditions in the ampule.

The calculations may be carried out in two ways: (1) by using a "free energy minimization" approach,[37−40] and (2) starting from the independent heterogeneous and homogeneous equilibria (K_P method), which are necessary to completely describe the system, a set of i nonlinear equations are set up individually for the source and sink region:

$$\Delta_R G°_{i,T} = - RT \ln K_{i,P,T} \qquad \text{(III.2)}$$

where $\Delta_R G°_{i,T}$ stands for standard free energy of reaction i at temperature T; $K_{i,P,T}$, equilibrium constant of reaction i at temperature T; and R, universal gas constant.

The temperature dependency of the equilibrium constant is described by the following relation:

$$\log K_{i,P,T} = \frac{A}{T} - B - C \log T \qquad \text{(III.3)}$$

where A, B, C are constants.

On the basis of the thermochemical data the system of i nonlinear equations can be solved by a Gauss−Newton-type method or a different iterative procedure (cf., Binnewies[41]).

Independent of a heterogeneous or homogeneous phase in the source, the simple concepts, however, fail to predict the kinds of deposited condensed phases in the sink. Nor will they work if the composition of the gas and the condensed phase change during the transport process ("nonstationary transport") and if the deposited phase in the sink and the remaining solid in the source have a homogeneity range.

This insufficiency led to the development of several other models: the cooperative transport model (Schweizer and Gruehn[42,43]); the concept of connecting the source and the sink zone by the so called ϵ-relation (Krabbes *et al.*[44,45]); and the four-stage model (Piekarczyk[46,47]).

2. The Cooperative Transport Model

A model ampule is hypothetically partitioned into two parts (source and sink). According to Schweizer and Gruehn,[42,43] a system with fixed starting parameters [total pressure $\sum p$, mean transport temperature $\bar{T}$, and starting materials (molar numbers of condensed phases and gaseous species)] is heated to the temperature of the source (i.e., T_2 for an endothermic transport reaction) and the composition of the resulting equilibrium gas phase is computed. The reaction may be congruent or incongruent. Under constant total pressure ($\sum p(\text{sink}) = \sum p(\text{source})$) the gas phase is hypothetically shifted from T_2 to T_1. This means, for an endothermic transport reaction ($T_2 \rightarrow T_1$, $T_2 > T_1$), that it must be cooled down from T_2 to T_1. Under these conditions the gas phase initially is metastable, leading to the establishment of a new equilibrium at T_1, which can be achieved by condensation of one or more solid and liquid phases, respectively.

Thus the cooperative transport model describes a stationary state by coupling the two subvolumes of the ampule by means of identical mass balance of source and sink. In contrast to Schäfer's K_P method[1] it is possible to calculate the transport of heterogeneous phases as well as gas phases of complicated composition.

The number of participating condensed phases differing during the transport process is taken into account by the iteration method of Schmidt and Gruehn.[48,49] According to the cooperative transport model the composition of the equilibrium gas phase and the condensed phases of the source are calculated and the gas phase is shifted to the sink. After the condensation of one or more phases the corresponding equilibrium gas phase of the sink is transferred back to the source. In order to restore the state of equilibrium at the source again a part of the condensed phases has to be dissoluted in the gas phase. After shifting this gas phase back into the sink and deposition of the condensed phases these are added to the already deposited sink solid. The iteration steps are repeated until the composition of the equilibrium gas phases and of the condensed phase at T_{source} and T_{sink} do not change any further.

Thus one can obtain transport rates and amounts of deposited condensed phases, e.g., for the following systems: $Si/SiAs/I_2/H_2O$,[31] $Si/SiAs/As/H_2O$,[50] $Ti/O/Hg/Cl$,[51] $Ti/O/Te/Cl$,[51] $VP/I_2/H_2$,[52] $V_2O_5/NH_4Cl/H_2O$,[53] $Cr_2O_3/CrOCl/Cl_2/H_2O$,[13,54] $Cr_2O_3/Br_2/H_2O$,[55] $Cr_2O_3/CrBr_3/Br_2/H_2O$,[55] $Cr_2O_3/HgCl_2/H_2O$,[54] $Cr_2O_3/CrI_3/I_2/H_2O$,[56] $CrP/CrI_2/I_2/H_2$,[57] $CrBr_3/Br_2/H_2O$,[58] $MnP/MnI_2/I_2/H_2$,[57] $CoP/CoI_2/I_2/H_2$,[12] $Mo/MoBr_2/HgBr_2/H_2O$,[10] $MoO_2/Mo_4O_{11}/HgCl_2/H_2O$,[59] $MoO_2/Mo_4O_{11}/HgBr_2/H_2O$,[60] $Eu/Al/Cl$,[61] $W/WO_2/HgBr_2/H_2O$,[11] $WO_2/HgCl_2/H_2O$,[62] $WO_2/HgBr_2/H_2O$,[14,62] $WO_2/W_{18}O_{49}/HgI_2/H_2O$,[63] $WO_3/HgCl_2/H_2O$,[64] $Rh_2O_3/RhCl_3/Cl_2/H_2O$,[15] $ScNbO_4/Cl_2/H_2O$,[65] $ScNbO_4/NbCl_5/Cl_2/H_2O$,[65] $MnNb_2O_6/Cl_2/H_2O$,[66] $MnNb_2O_6/NH_4Cl/H_2O$,[66] $CoNb_2O_6/Cl_2/H_2O$,[67] $CoNb_2O_6/NH_4Cl/H_2O$,[67] $CoNb_2O_6/HgCl_2/H_2O$,[67] $NiNb_2O_6/Cl_2/H_2O$,[68] $NiNb_2O_6/NH_4Cl/H_2O$,[68] $Ga_2(SO_4)_3/HCl/H_2O$,[69] $Ga_2(SO_4)_3/Cl_2/H_2O$,[69] $In_2(SO_4)_3/HCl/H_2O$,[70] $FeSO_4/NH_4Cl/H_2O$,[71] $Fe_2(SO_4)_3/Cl_2/H_2O$,[71] $Fe_2(SO_4)_3/HCl/H_2O$,[72] $Fe_2(SO_4)_3/NH_4Cl/H_2O$,[71] $Cr_2(SO_4)_3/Cl_2/H_2O$,[73] and $Cr_2(SO_4)_3/HCl/H_2O$.[73]

3. Solid-State Composition at Steady-State Transport

To describe the transport of several solids with a homogeneity range as well as ternary solid solutions a general model was developed by Krabbes *et al.*[44,45,74] Presuming an equilibrium state in the source and the sink zone caused by a congruent or incongruent reaction of the starting solid with the transport agent, it is possible to calculate the composition of the equilibrium solids (AB_x (T_{source}) and AB_x (T_{sink})) and the corresponding transport rates.

Some of the components of the system only occur in the gas phase (solvent components) others are present in both states of aggregation, i.e., gaseous and condensed states. In this model the authors take all elements as components.

Both equilibrium zones are connected by ($n - 1$) relations of the type[44,45,74]

$$\epsilon^{(B)} = \left(\frac{P_B^*}{P_L^*}\right)_{T_{source}} - x_{T_{source}}\left(\frac{p_A^*}{p_L^*}\right)_{T_{source}} = \left(\frac{P_B^*}{P_L^*}\right)_{T_{sink}} - x_{T_{sink}}\left(\frac{p_A^*}{p_L^*}\right)_{T_{sink}} \qquad \text{(III.4)}$$

where p_K^* stands for the equilibrium pressure of the component K (components A or B of the condensed phase or the solvent component L); T_{source}, temperature of the source; T_{sink}, temperature of the sink; and x_T, composition of the solid at T_{source} or T_{sink}; and

$$p_K^* = \sum_{i=1}^{l} \alpha_{k,i} p_i \qquad \text{(III.5)}$$

where $\alpha_{k,i}$ stands for stoichiometric index of the component K in ith species; and p_i, partial pressure of the species i.

This model explains the transport behavior of several systems containing phases with homogeneity ranges as well as the subsequent transport in multiphase systems: $Ga_2O_3/TeCl_4$,[75] $TiB_2/TiBr_4$,[76] TiB_2/BBr_3,[76] Te/O/Cl,[77] Ti/O/C/Cl,[78] Ti/Si/X (X = Cl, I),[79] VO_2/Cl_2,[80] $VO_2/HCl/Cl_2$,[80] V/O/Te/Cl,[81,82] V/Si/Cl,[83] Mn/O/X (X = Cl, Br),[84] Mn/O/H/X (X = Cl, Br, I),[84] $MnO_2/InCl_3/Cl_2$,[85] Mn/O/M/Cl (M = Te, Se),[86] $MnCl_2/MCl_3$ (M = Al, Ga, In),[87] Fe/O/Cl,[88] Fe/O/H/Cl,[80] FeS_x/I_2,[89,90] Fe/S/H/Cl,[91] Fe/S/N/H/Cl,[91] CoS/HI,[92] CoS/I_2,[92] Ni/S/N/H/I,[92] $M/S/GeI_2$ (M = Fe, Ni),[91] M/S/X (M = Fe, Ni; X = Cl, I),[91] Cu/O/H/Cl,[93] Cu/O/H/N/Cl,[94] Nb/O/Te/Cl,[95,96] $NiTiO_3/SeCl_4$,[97] $Co_yFe_{1-y}S_x/NH_4I$,[92] $Co_yFe_{1-y}S_x/GeI_2$,[92,98] $Fe_{1-y}Ni_yS_x/I_2$,[91] $Fe_{1-y}Ni_yS_x/GeI_2$,[91,98] $Zn_{1-y}Co_yO/Br_2$,[98] Mn/Mo/O/Cl,[99] Mn/Mo/O/Cl/H,[99] Mn/Mo/O/Cl/Te,[99] Cu/Mo/O/H/Cl,[100] $Y_3Fe_5O_{12}/CCl_4$,[101] Ru/V/O/Cl/Te,[102,103] Ru/Ti/O/C/Cl,[102] and Ga/V/O/Cl/Te.[102]

4. The Four-Stage Model

On the basis of four consecutive cycles, Piekarczyk[46,47] described the chemical transport of condensed phases with fixed stoichiometry as follows: (i) volatilization of the condensed phase in the dissolution zone leading to an equilibrium between the condensed phase and the gas phase; (ii) migration of the gas phase from the dissolution zone at T_{source} to the deposition zone and supersaturation at T_{sink}; (iii) deposition of the condensed phase at the sink; and (iv) migration of the gas phase back to the source.

It is assumed that the mass transport proceeds by thermal convection as long as the total pressure is very high (molecular diffusion, thermodiffusion, and Stefan flow[104] are neglected). Thus no transport rates and no transport mechanisms are computed.

The model is intended to calculate the kind of deposited phases at T_{sink}. Because the gas phase is shifted from T_{source} to T_{sink} in stage ii equilibrium conditions no longer exist. For this calculation Piekarczyk assumes a certain supersaturation of the gas phase at the end of the stages ii and iii. As a result the composition of the gas phase changes by homogeneous reactions of the gaseous species. Since it is presumed that no condensed phase is precipitated, the gas phase is supersaturated with regard to the solid(s). Thus the kind of the eventually deposited solid can be derived in analogy to the paper of Gruehn and Schweizer.[42]

The four-stage model was applied in the transport systems C/H,[105,106] $NiTiO_3/SeCl_4$,[97] $ZnCr_2O_4/Cl_2$,[47] $Y_3Fe_5O_{12}/Cl_2$,[47] $Y_3Fe_5O_{12}/CCl_4$,[47] and $Fe_2TiO_5/FeCl_3/Cl_2$.[47]

C. Calculation of the Mass Flux

Various concepts were developed to calculate the mass flux. The principles of these models are briefly outlined here.

1. Diffusive Transport Model by Schäfer

Following Schäfer's model[1,107,108] a transport reaction is defined as a reaction of a solid or liquid with a gaseous component in a temperature gradient to form exclusively gaseous products. Hence a gas phase consisting of only of two components (gaseous species B_g and C_g) may be described with

$$iA_s + kB_g = jC_g \qquad \text{(III.6)}$$

The transport of the substance A is caused by a difference of partial pressures Δp_c of the gaseous species C_g between the source region (site of dissolution of the condensed phase in the gas phase) and the sink region (site of deposition of the condensed phase out of the gas phase).

For the chemical transport caused only by diffusion, like in a sealed silica ampule, Schäfer obtained the transport equation (eq III.7) for the migration of the solid A in a one-dimensional system. In such a system it is assumed that diffusion only proceeds parallel along the long axis of the ampule. Provided that the gas phase as a whole does not move from the source to the sink [which is true of reactions without a change in the number of moles ($j = k$)] the amount of transported solid A (mole) is calculated to be (convection and thermodiffusion is neglected)

$$n_a = \frac{i}{j}\,\frac{\Delta p_c \bar{T}^{0.8} q t}{\sum p s}\, 1.8 \times 10^{-4} \quad \text{(mol)} \qquad \text{(III.7)}$$

where i and j stand for coefficients of the reaction equation; $\bar{T}$, average temperature of the diffusion path ("mean transport temperature"; $\bar{T} = {}^1/_2(T_2 + T_1)$) ($K$); q, cross section of the diffusion path (cm^2); t, transport time (h); Δp_c, difference in equilibrium pressure (atm); $\sum p$, total pressure in the tube (atm); and s, length of diffusion path (cm). The coefficient 1.8×10^{-4} is only valid for variables p, q, t, and s as given in the noted units. Furthermore it describes the pressure and temperature dependency of the average diffusion coefficient D using an average standard diffusion coefficient $D_o = 0.1$ cm^2/s at $T = 298$ K and $p = 1$ atm.

The diffusive transport model by Schäfer was applied to the transport systems MgO/HCl,[109] GaAs/I_2,[110] GaSe/I_2,[111] In_2S_3/I_2,[112] TiS_2/I_2,[113] V/Se/I,[114] $CrCl_3/Al_2Cl_6$,[115] $FeCl_2$/HCl,[116] FeP_2/I_2,[117] NiO/HCl,[109] $NiCl_2$/HCl,[116] Cu_2O/HCl,[118] $LaPO_4/Br_2$,[19] $LaPO_4/Br_2/PBr_3$,[19] $LaPO_4$/HBr,[19] $NiFe_2O_4$/HCl,[119] $GeSe_{0.99}Te_{0.01}/GeI_4$,[122] $GeSe_{0.98}Te_{0.02}/GeCl_4$,[122] and GeS/$GeCl_4$/Ar.[122]

2. Diffusive Transport Model by Lever

For a one-dimensional system, Lever[120] described the chemical transport of only one solid involving several simultaneous heterogeneous and homogeneous equilibria.

In this paper a simple expression for the concurrent diffusive transport of several gaseous species by a common binary diffusion coefficient for each pair of gases is used. Diffusion and net drift of the gas phase (Stefan flow[104]) are taken into account. By using all binary diffusion coefficients one mean diffusion coefficient D is estimated for the whole transport system.

The chemical elements present in the system are labeled A, B, C, ..., L, ..., the molecular species 1, 2, 3, ..., λ, ..., and a molecule of species λ contains a_λ atoms of A, b_λ of B, ..., and l_λ of L ..., etc. The molar density of the species λ in the gas phase is n_λ (mol/cm^3) and the density n_L (g atoms/cm^3) of the element L is given by

$$n_L = \sum_\lambda l_\lambda n_\lambda \qquad \text{(III.8)}$$

where l_λ stands for stoichiometric coefficient of the element L in the molecule species λ; and n_λ, molar density of the molecule species λ.

By defining a value η_L for the element L

$$\eta_L = n_L/n_V \qquad \text{(III.9)}$$

where n_L stands for the gram atomic density of the component L in the gas phase; and n_V, total gram atomic density of the solvent atoms in the gas phase (the solvent atom is not present in the solid), he obtained for the flux J_L (mol/cm^2 s) of the element L

$$J_L = nD\,\frac{n_v^*}{n}\left[\frac{\eta'_L - \eta''_L}{x' - x''}\right] \qquad \text{(III.10)}$$

with

$$(n_v^*)^{-1} = (x' - x'')^{-1}\int_{x''}^{x'}\frac{dx}{n_v} \qquad \text{(III.11)}$$

where η'_L and η''_L stand for η_L at x'' or x'; n, total molar density of the gas phase ($\sum_\lambda n_\lambda$); D, mean diffusion coefficient; x'', location of the source; and x', location of the sink.

The model was applied to the transport systems Ge/GeX_4 (X = Br, I),[121] $GeSe_{0.99}Te_{0.01}/GeI_4$,[122] $GeSe_{0.98}Te_{0.02}/GeCl_4$,[122] and GeS/$GeCl_4$/Ar.[122]

3. Diffusive Transport Model by Mandel

By assuming a one-dimensional system[123] in which there are M species (gaseous species $G_{i,g}$ and the only condensed species S_s) present with C conservation conditions, $N = M - C$ independent, simultaneously operating chemical equilibria have to be specified. The jth of these N equilibria may be expressed as follows

$$S_s + aA_g = bB_g + cC_g + dD_g + \ldots \qquad \text{(III.12)}$$

and more generalized

$$S_s = \sum_{i=1}^{M-1} q_{ij} G_{i,g} \qquad \text{(III.13)}$$

where S_s stands for condensed phase; q_{ij}, reaction coefficient for gaseous species i in reaction j; and $G_{i,g}$, the ith gaseous species.

After Mandel[123] in this system the flux F_s (mol/cm^2 s) of the solid S can be calculated by defining a set of $N - 1$ coupling parameters $\bar{\alpha}_2, \bar{\alpha}_3, \ldots, \bar{\alpha}_N$ to be

$$F_s = \frac{\Delta H_1 \Delta T}{R^2 \bar{T}^3 L}\left(1 + \sum_{j=2}^{N}\bar{\alpha}_j\right)(\phi_{11} + \bar{\alpha}_j\phi_{12} + \ldots + \bar{\alpha}_N\phi_{1N})^{-1} \qquad \text{(III.14)}$$

where $\bar{\alpha}_j$ is defined as

$$\bar{\alpha}_j = \frac{|[-\phi_{11} + (\Delta H_1/\Delta H_n)\phi_{n1}]|}{|[-\phi_{1t} + (\Delta H_1/\Delta H_n)\phi_{nt}]|} \qquad \text{(III.15)}$$

where ΔT stands for temperature difference between source and sink ($= T_2 - T_1$); R, universal gas constant; $\bar{T}$, mean transport temperature ($= {}^1/_2(T_2 + T_1)$); L, distance between source and sink; ΔH_i, enthalpy change of the transport equilibrium ($1 \leq i \leq n$); and ϕ_{nt} is given by

$$\phi_{nt} = \sum_i \frac{q_{in}}{\bar{p}_i}\left\{\sum_j\left(\frac{q_{jt}\bar{p}_i - q_{it}\bar{p}_j}{p\bar{D}_{ij}}\right)\right\} \qquad \text{(III.16)}$$

where q_{in} stands for reaction coefficient for species i in reaction n; $\bar{p}_i$, average partial pressure of the species i; q_{jt}, reaction coefficient for species j in reaction t; q_{it}, reaction coefficient for species i in reaction t; $\bar{p}_j$, average partial pressure of the species j; p, total pressure; and D_{ij}, diffusion coefficient of a binary mixture of components i and j.

In earlier papers[124,125] it was shown that the migration of a solid may be explained exclusively by diffusion; viscous flow ("streaming"), convection, and thermal diffusion are neglected. The binary diffusion coefficients have to be evaluated from the literature data or by calculation. The theory was applied to the transport systems ZnS/HCl,[126] ZnS/I_2,[127] CdS/I_2,[128,129] CdTe/I_2,[130] CdTe/NH_4Cl,[131,132] YbAs/I_2,[133] $GeSe_{0.99}Te_{0.01}/GeI_4$,[122] $GeSe_{0.98}Te_{0.02}/GeCl_4$,[122] and GeS/$GeCl_4$/Ar.[122]

4. The Concept of the Solubility of a Condensed Phase in the Gas Phase

The simple method described above can only be used when only one identical phase is present in both sink and source and when only one heterogeneous equilibrium is causing the transport.

When the transport is caused by two or more transport equilibria for identical phases in source and sink, Schäfer[134] developed the concept of "solubility" in the gas phase. Hence, the solubility λ_i of a condensed phase or element i is defined as follows

$$\lambda_i = \frac{\text{amount of } i}{\text{amount of solvent component } L} = \frac{\sum n_i}{\sum n_L} = \frac{\sum p_i}{\sum p_L} \qquad \text{(III.17)}$$

On the basis of this concept it is possible to calculate the amount n_a (mol) of transported solid A for chemically more complicated systems, including systems with changing numbers of gas molecules depending on the temperature

$$n_a = \Delta\lambda_i \frac{\sum p(\mathrm{L})\bar{T}^{0.8} q t D_o}{\sum p s} 1.8 \times 10^{-3}\ \text{(mol)} \qquad \text{(III.18)}$$

where $\Delta\lambda_i$ stands for λ_i(source) − λ_i(sink), difference in solubility of the element i between source and sink; $\sum p(\mathrm{L})$, arithmetical mean of the total equilibrium pressures of the solvent atoms at the source and sink $^1/_2$ $(\sum p(\mathrm{L})_{\mathrm{source}} + \sum p(\mathrm{L})_{\mathrm{sink}})$; $\bar{T}$, average temperature of the diffusion path ("mean transport temperature" $^1/_2$ $(T_2 + T_1)$); D_o, average diffusion coefficient at $T = 298$ K and $p = 1$ atm; q, cross section of the diffusion path; t, transport time; $\sum p$, total pressure in the tube; and s, length of diffusion path. For comments on the coefficient 1.8×10^{-3} see section III.C.1.

The concept was applied to the transport systems Si/I_2,[134] $Si/SiCl_4$,[134] Ga_2O_3/Cl_2,[135] $Ga_2O_3/H/Cl$,[136] $GaAs/I_2/H_2$,[134] Ge/I_2,[137] Ge/H_2O,[48] $Ge/GeCl_4$,[138] In_2O_3/Cl_2,[139] SnS_2/I_2,[140] $Sb/SbCl_3$,[141] $Sb/GaCl_3$,[141] Sb_2S_3/I_2,[142] TiO_2/XCl_4 (X = Te, Se, C),[143] $MnCl_2/MCl_3$ (M = Al, Ga, In),[87] Fe/HCl,[134] Fe_2O_3/HCl,[134] $Fe_2O_3/TeCl_4$,[144] $FeS/H/X$ (X = Cl, Br, I),[145] FeS/MX_4 (M = Ge, Sn; X = Cl, I),[145] Ni/CO,[146] $MoCl_3/Cl_2$,[147] Ag/I_2,[148] Ta_2O_5/S_2,[149] TaS_2/S_2,[150] $W/Cl_2/Ar$,[134] $ReO_2/Re_2O_7/HCl$,[134] Pt/Cl_2,[151] $M/GaCl_3$ (M = Fe, Co, Ni),[152] MCl_2/Al_2Cl_6 (M = Co, Ni, Cu),[153] MCl_2/Al_2Cl_6 (M = Ca, Cr, Fe, Co, Ni, Cu, Pd),[154] $Co/Ni/GaI_3/I_2$,[155] and $Cu/Ag/I_2$.[156]

By using the model of Krabbes *et al.*[44,45] it is possible to calculate the transport rate $\dot{n}$ (mol/s) of a solid based on the concept of the solubility in the gas phase with the formula

$$\dot{n}(\mathrm{AB}_x\mathrm{C}_y...) = \bar{p}^*(\mathrm{L}) \frac{\bar{T}^{0.8} a \bar{D}_o}{p_{\mathrm{tot}} \Delta l} 1.8 \times 10^{-3} \left\{ \left(\frac{p^*_{\mathrm{A}}}{p^*_{\mathrm{L}}}\right)_{T_{\mathrm{source}}} - \left(\frac{p^*_{\mathrm{A}}}{p^*_{\mathrm{L}}}\right)_{T_{\mathrm{sink}}} \right\} \qquad \text{(III.19)}$$

where $\bar{D}_o$ stands for mean diffusion coefficient; $\bar{T}$, mean temperature; a, cross section of the ampule; p_{tot}, total pressure; Δl, length of the ampule; $\bar{p}^*$, mean solvent balance pressure; and $\bar{p}^*_{\mathrm{K}}$, balance pressures of the components A and B of the condensed phase or the solvent component L. For comments on the coefficient 1.8×10^{-3} see section III.C.1.

The concept of solubility in the gas phase by Schäfer is the fundamental principle of the programs EPDELT[157] and EPLAM,[157] respectively, yielding the transport rates given in the papers listed in section III.B.2.

5. Diffusive Transport Model by Arizumi and Nishinaga

Arizumi and Nishinaga[158−160] proposed transport equations for the transport of materials (semiconductors) in closed tubes assuming a one-dimensional system and considering diffusion and laminar flow as the fundamental transport mechanism (AN model). These equations can be applied to transport systems containing foreign matter, as well.

For the element and the compound semiconductors, the reactions are expressed by

$$\mathrm{A}_{i,\mathrm{s}} + m_i\mathrm{I}_{2,\mathrm{g}} = \mathrm{A}_i\mathrm{I}_{2m_i,\mathrm{g}} \qquad \text{(III.20)}$$

For some compound semiconductors the reactions are described by

$$\mathrm{A}_i\mathrm{B}_{\mathrm{h,s}} + m_i\mathrm{I}_{2,\mathrm{g}} = \mathrm{A}_i\mathrm{I}_{2m_i,\mathrm{g}} + 1/y\mathrm{B}_{\mathrm{h}_y,\mathrm{g}} \qquad \text{(III.21)}$$

The flux rate n_x (mol/cm^2 s) of the ith element x (i = 1, 2, ..., v) is given by

$$n_x = \frac{1}{R\bar{T}} \sum_{i=1}^{v} \left(-D_i \frac{\mathrm{d}P_i}{\mathrm{d}X} + \frac{P_i \sum D_i m_i \left(\frac{\mathrm{d}P_i}{\mathrm{d}X}\right)}{\sum m_i P_i} \right) \qquad \text{(III.22)}$$

The following simplifications are used to solve expression (III.22):

$$\frac{\mathrm{d}P_i}{\mathrm{d}X} = \frac{P_i^{(1)} - P_i^{(2)}}{L} = \frac{\Delta P_i}{L} \qquad \text{(III.23)}$$

and

$$P_i = \frac{P_i^{(1)} + P_i^{(2)}}{L} \qquad \text{(III.24)}$$

where $\bar{T}$ stands for average temperature along the transport distance; R, universal gas constant; D_i, diffusion coefficient; $P_i^{(n)}$, partial pressure of element i at source ($n = 1$) or sink ($n = 2$); X, position variable; m_i, reaction coefficient of element i; and L, transport distance.

The AN model was applied in the transport systems GaS/I_2,[161] $GaAs/I_2$,[158] Ge/I_2,[158] $Ge/P/I_2$,[158] $GaAs/Ge/I_2$,[159] $ZnO/HgCl_2/H_2O$,[162] ZnS/NH_4Cl,[163] $ZnSe/I_2$,[164] $ZnTe/I_2$,[165−167] $ZnTe/HCl$,[168] CdS/I_2,[168] $CdTe/I_2$,[130,169] $ZnTe/GaAs/I_2$,[170] and $ZnTe/Ge/I_2$.[165,171]

6. Transport Model by Factor and Garrett

Following the model of Factor and Garrett,[28] in a one-dimensional transport system the flux rate J (mol/cm^2 s) of a component i caused by diffusion and Stefan flow[104] can be described as follows

$$J = \frac{DP}{RTl} \ln \left\{ \frac{p(l) - P}{p(0) - P} \right\} \qquad \text{(III.25)}$$

where D stands for the diffusion coefficient; P, total pressure; R, universal gas constant; T, average temperature along the transport distance; l, transport distance; $p(l)$, partial pressure at l (sink); and $p(0)$, partial pressure at $l = 0$ (source).

The transport model of Factor and Garrett was applied to the transport systems $GaAs/HCl$,[172,173]

$ZnSe/I_2$,[174] $HgZnTe/HgI_2$,[175] $GeSe_{0.99}Te_{0.01}/GeI_4$,[122] $GeSe_{0.98}Te_{0.02}/GeCl_4$,[122] and $GeS/GeCl_4/Ar$.[122]

7. The Flux Function Method of Richardson and Noläng

By defining flux functions Φ of the condensed phases it is possible to calculate net fluxes J_k (mol/cm^2 s) of these phases based on an equilibrium model.[176−178] The flux function takes into account the Stefan flow,[104] as well as the temperature and total pressure variation of the diffusion coefficient. Thus it becomes possible to compute the transport rates of the simultaneous migration of several condensed phases, of condensed phases with incongruent vaporization or with variable composition in a one-dimensional system.

A flux function Φ takes the temperature dependency of the diffusion coefficient into account. The advantage of this flux function is, that different transport systems with different transport agents, temperature gradients and diffusion coefficients can be compared to each other (e.g., transport of SnO_2—a comparison of 30 different transport agents[177]). It is defined by

$$\Phi = \frac{J_k}{\left(\bar{D}_o \dfrac{dT}{dx}\right)} \qquad (III.26)$$

where $\bar{D}_o$ stands for the mean average diffusion coefficient; dT/dx, temperature gradient; and J_k, net flux of the condensed phases ($k = 1, 2, ..., l$).

The fluxes J_k ($k = 1, 2, ..., n$) of the condensed phases are related to the fluxes J_j of the elements ($j = 1, 2, ..., n$) by the equation

$$J_j = \sum_{k=1}^{n} \lambda_{kj} J_k \qquad (III.27)$$

where λ_{kj} stands for the stoichiometric coefficient of the jth element ($j = 1, 2, ..., l$) in the condensed phase k; and J_k, net flux of the condensed phases ($k = 1, 2, ..., l$), with

$$J_j = -\frac{\bar{D}_o p_0 T^{\alpha-1}}{R p_{tot} T_0^{\alpha}} \frac{dT}{dx} \sum_{i=1}^{m} \lambda_{ij} \left[\frac{dp_i}{dT} - p_i \frac{\sum_{i=1}^{m} \lambda_{ir} \dfrac{dp_i}{dT}}{\sum_{i=1}^{m} \lambda_{ir} p_i} \right] \qquad (III.28)$$

where $\bar{D}_o$ stands for mean average diffusion coefficient; p_0, pressure at T_0; T, temperature; α, empirical constant ($\alpha = 1.5-2.0$);[179] R, universal gas constant; p_{tot}, total pressure; T_0, reference temperature; dT/dx, temperature gradient; λ_{ij}, stoichiometric coefficient of the jth element ($j = 1, 2, ..., l$) in the gaseous species i; λ_{ir}, stoichiometric coefficient of the solvent element r in the ith species; p_i, partial pressure of the ith species ($i = 1, 2, ..., m$); and dp_i/dT, pressure gradient.

The partial pressures of the gaseous species i ($i = 1, 2, ..., m$) are calculated by the authors by minimization of the total Gibbs' free energy under mass balance conditions using for example the program SOLGASMIX.[180] The method was applied to the following transport systems: CoP_3/Br_2,[178] FeP/I_2,[178] FeS_2/X_2 (X = Cl, Br, I),[181] RuS_2/X_2 (X = Cl, Br, I),[182] Cu_6PS_5X/X_2,[183] HfS_2/X_2 (X = Cl, Br, I),[184] $CuInS_2/X_2$ (X = Cl, Br, I),[185] $Y_3Fe_5O_{12}/Cl_2$,[178] $Y_3Fe_5O_{12}/HCl$,[178] and $Ni_3B_7O_{13}Cl/Cl_2$.[186]

A critical comparison of the flux function method and experimental results are given by Krabbes *et al.* for the transport system $V_8O_{15}/VO_2/TeCl_4$.[89]

8. The Productivity Function of Klosse

Klosse[187] considers a chemical vapor transport system in which the transport of the condensed phase $A_{i,s(l)}$ (solid or liquid) and gaseous compounds $B_{i,g}$ is based on one or more independent reactions of the type

$$\nu_A A_{s(l)} + ... + \nu_B B_g + ... = \nu_C C_g + ... \qquad (III.29)$$

or more generalized

$$0 = \sum_i \nu'_{ri} A_{i,s(l)} + \sum_i \nu_{ri} B_{i,g} \qquad (III.30)$$

where ν'_{ri} stands for stoichiometric coefficient of the ith condensed phase $A_{i,s(l)}$ in reaction r; and ν_{ri}, stoichiometric coefficient of the ith gaseous compound $B_{i,g}$ in reaction r.

Klosse introduces the rate of reaction $\dot{\xi}$ (mol/s), which describes the unireactional diffusive transport in a one-dimensional system (the effects of finite interface kinetics is formally taken into account):

$$\dot{\xi} = -\frac{ODP}{lRT}\{(1-\alpha)\Delta \ln K\}F \qquad (III.31)$$

where O stands for the cross-sectional area of the ampule; D, diffusion coefficient; P, total pressure; l, length of the ampule; R, universal gas constant; T, absolute temperature; α, parameter to account interface kinetic constraints ($0 \leq \alpha \leq 1$); and K, equilibrium constant of the heterogeneous transport reaction ($\Delta \ln K = \ln K(T_{source}) - \ln K(T_{deposition})$).

For this a productivity function F has to be defined that is proportional to the crystal growth rate. The mole fractions of the gaseous species and the stoichiometric coefficients in the transport reaction are taken into account.

$$F = \left[\sum_i \frac{\nu_i^2}{x_i} - \left(\sum_i \nu_i\right)^2\right]^{-1} \qquad (III.32)$$

where ν_i, stands for the stoichiometric coefficient of the ith element ($i = 1, 2, ..., l$) in the condensed phase A_i; and x_i, mole fraction of the species i ($x_i = p_i/\sum_i p_i$).

The productivity function of Klosse was applied to the transport system ZnS/I_2.[188]

D. Model Calculations by Computer Programs

1. EPC, EPDELT, and EPLAM

Using the cooperative transport model, the program EPC[37,38,157,176,177,189] calculates the equilibrium conditions (condensed phases with the correlated gas phase). All occurring substances (condensed phases and gaseous species) have to be known. For a calculation EPC needs the thermodynamic data of all substances: standard enthalpy of formation $\Delta_B H°_T$, standard entropy $S°_T$, and heat capacity $C_P(T)$. Moreover the program requires a starting parameter list: starting substances i with mole numbers n_i, considered possible reaction products (condensed phases and gaseous species), temperature of sink and source, total pressure, and volume of the ampule.

With the given thermochemical data and starting parameters EPC calculates the position of equilibrium by means of minimization of the total free Gibbs energy $\Delta G°$ first for T_{source} and then for T_{sink}. The results of the calculation (amounts of condensed phases and gaseous species) are written to an output file.

Using the results of the EPC calculations the program EPDELT[157] calculates the differences of partial pressures Δp_i for all gaseous species. These are listed as values $\Delta p_i/\Sigma p$ (Σp = total pressure) for each element occurring in the system. It is also possible to calculate the transport rates of a substance by EPDELT. Gaseous species which migrate from the source to the sink get a positive $\Delta p_i/\Sigma p$ value, while species with an opposite migration direction (sink → source) have values less than zero. Because of the standardization of the $\Delta p_i/\Sigma p$ values to each element, it is possible to obtain information on the flux of the solid from these results.

By using the program EPLAM[157] it is possible to compute solubilities of gaseous species at T_{source} and T_{sink} and from these values the differences of solubilities $\Delta\lambda_i$.[134] For this it is necessary to define the solvent element in a separate file.

2. Nonstationary Model Calculation

By using the program EPCBAT,[190] it is possible to make model calculations for several consecutive steady states according to the iteration method of Schmidt and Gruehn.[48,49] This can be achieved by several successive EPC calculations.

After the first EPC calculation (computing of the condensed phases and the corresponding equilibrium in the gas phase at T_{sink} and T_{source}) the amount of the deposited condensed phase in the sink is subtracted from that of the condensed phase in the source. After this a new EPC calculation is started. In every following cycle the mass of the condensed phase of the source is diminished by the deposit at the sink.

When one condensed phase has been completely transported to the sink, a subsequent steady state may occur. This is indicated by changes in equilibrium gas-phase composition.

For every cycle an EPDELT calculation can be done to get information of the changes in the transport model during the transport experiment.

3. CVTrans

CVTrans[191] is WINDOWS based and developed from the older program package EPC, EPDELT, and EPCBAT.[37,38,157,176,177,189,190] It calculates the composition of the condensed and gas phase under equilibrium conditions by minimization the free enthalpy of a system according to a procedure by Eriksson.[37] The composition of the condensed and the gas phase of source and sink region are related to each other by applying the cooperative transport model by Schweizer and Gruehn.[42,43]

The mass transfer between source and sink (deposition rates) is calculated using the concept of Schäfer.[134]

4. GMIN

The solid-state composition at steady state (Krabbes *et al.*[44,45]) can be computed by using the computer program GMIN[192] (the program GMIN is part of the program package TRAGMIN). The program calculates, by minimization of the Gibbs free energy (iterative procedure given by Erikson[37]), the equilibrium partial pressures of the species i and the equilibrium condensed phases with their corresponding compositions using one (or more) ϵ relations (eq III.4). Generally it is possible to choose between four models describing the relationships between the solids of a transport system: (1) binary condensed phases of the type AC_x ($x = n_C/n_A$); (2) ternary (quasi-binary) condensed phases $A_yB_{1-y}C_x$ with or without miscibility gap, which can be described as regular solutions of the two end members (binary phases AC_x and BC_x, $yAC_{x,s} + (1 - y)BC_{x,s} = A_yB_{1-y}C_{x,s}$); (3) binary systems with the condensed phase AC_x containing the component A in ith highest state of oxidation (in contrast to model 1 and 2 the activity of C in the solid is described by a different model[192]); and (4) ternary (quasi-binary) condensed phases whose end members can be described similar to model 3.

GMIN needs the thermochemical data of all condensed phases (end members of the homogeneity range) and gaseous species as follows: standard enthalpy of formation $\Delta_B H°_T$, standard entropy $S°_T$, heat capacity $C_P(T)$, and activity a_C of the component C in phases AC_x or $A_yB_{1-y}C_x$.

Furthermore the molar ratio of the components, the volume, the pressure, and the temperature have to be fixed.

It is possible to create gas-phase plots (partial pressures of gaseous species i as functions of temperature) or the solubilities defined by Schäfer[134] by the subprogram GASGRAPH and to calculate the transport rate by the subprogram TRANS (both parts of the program TRAGMIN).

E. Convection

In the above-described transport models the flux of a solid is calculated by assuming diffusion and Stefan flow[104] as mass-transfer processes. In chemical transport reactions convection is naturally involved in the mass flux. It has been observed that for high pressures ($p > 1$ atm) and special ampule shapes l/h (l = length and h = height of the ampule) the transport rate is increased. We distinguish between forced convection, which is caused by the influence of a gravitational field on a thermal or concentration gradient, and free convection (locally imposed motion).

In typical transport experiments (horizontal position of the transport ampule with respect to the gravitation vector) at higher total pressures convection increases the transport rate. Such effects on the transport rates were investigated in the transport systems $GaAs/HCl$,[173] Ge/I_2,[137,193−196] Ge/GeI_4,[197] $Ge/GeCl_4$,[138] $GeSe/GeI_4$,[198] $GeTe/GeI_4$,[198] SnS_2/I_2,[199] SnS_2/SnI_4,[199] $Sb/GaCl_3$,[141] Ni/CO,[200−202] $MnS/MnSe/I_2$,[203]

ZnS/I_2,[126,204,205] $ZnSiP_2/I_2$,[206] $YbAs/I_2$,[133] TaS_2/S_2[150] and $Hg_{1-x}Cd_xTe/HgI_2$.[7,207,208] A general treatment of this problem was given by Schäfer *et al.*,[107] Reed *et al.*,[209] and Curtis and Dismukes.[210]

The growth of crystals and epitaxial layers is influenced by convection, too. Investigations of the effects on the morphology of crystals and layers grown by chemical transport reactions under the influence of convection are reported in the transport systems $GaAs/GaI_3$,[211] $GeSe/GeI_4$,[212,213] $Hg_{1-x}Cd_xTe/HgI_2$,[214−218] $GeSe/I_2$,[219] $GeSe_2/I_2$,[219] $GeTe/I_2$,[219] $GeTe/GeI_4$,[213] $ZnTe/I_2$,[220] $MnSe/CdSe/I_2$,[221] $GeSe_{0.99}Te_{0.01}/GeI_4$,[122] $GeSe_{0.98}Te_{0.02}/GeCl_4$,[122] and $GeS/GeCl_4/Ar$.[122]

A more general theoretical treatment of convection is given by Carruthers,[222,223] Launay and Roux,[224] Reed *et al.*,[209] and Rosenberger *et al.*[225−230]

There is only one attempt at a detailed analysis of convective flow given by Klosse and Ullersma[231] (KU model). They assumed a two-dimensional rectangular enclosure with two vertical walls. According to this model natural convection is effected by a temperature gradient only. The mass flux F^* (mol/cm^2 s) is given by the following equation:

$$F^* = F(K + 1) \qquad \text{(III.33)}$$

where F stands for the mass flux caused by diffusion with

$$\frac{1}{K} = \left[A\left(\frac{D_o}{p^2 d^3}\right)^2\left(\frac{R\bar{T}^2\mu}{\bar{M}g\Delta T}\right)^2 + B\right] \qquad \text{(III.34)}$$

where A and B stand for dimensionless quantities depending on the geometry of the ampule (see ref 231); D_o, average diffusion coefficient; p, total pressure; d, ampule diameter; R, universal gas constant; $\bar{T}$, average temperature; μ, average viscosity of the gas phase; $\bar{M}$, average molar weight of the gas phase; g, gravitational force; and ΔT, temperature difference between source and sink.

The average viscosity of the gas phase μ is calculated to be

$$\mu = \sum_{i=1}^{n}\left(\frac{x_i\mu_i}{\sum_{j=1}^{n} x_j\Phi_{ij}}\right) \qquad \text{(III.35)}$$

where x_i and x_j are molar fractions of the gaseous species i,j; μ_i and μ_j, viscosities of the gaseous species i and j (which can be taken from the literature) with

$$\Phi_{ij} = \frac{1}{\sqrt{8}}\left(1 + \frac{M_i}{M_j}\right)^{-1/2}\left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{1/2}\left(\frac{M_j}{M_i}\right)^{1/2}\right]^2 \qquad \text{(III.36)}$$

where M_i and M_j are molar weights of the gaseous species i,j.

The KU model was applied to the transport systems $GaSe/I_2$,[111] $GeSe/GeI_4$,[36,232,233] ZnS/NH_4Cl,[163] $ZnSe/I_2$,[164,174] $ZnTe/I_2$,[167] $ZnTe/HCl$,[168] CdS/I_2,[128,234] $CdTe/I_2$,[130,169] and $CdTe/HCl$.[235]

A review on convection is given by Solan and Ostrach.[236]

IV. Remarks and Comments on the Calculation Procedure

When a chemist is interested in calculating the transport process that he possibly has investigated by experiments some general aspects have to be taken into account.

At first he has to prove the transport system is well described by thermochemical data of all phases (condensed and gaseous). Often the composition of the gas phase is a great problem. In many systems the gas phase is not completely investigated. An unidentified gaseous species may prevent the description of the transport behavior of a condensed phase. Therefore we have chosen the chromium, molybdenum, and tungsten containing systems for our paper, because these systems are very well described and the thermodynamical data are well known. Some of the compounds are of great interest because of their physical properties. In the past the crystallization of these were often carried out by chemical transport reactions.

Simple systems with only one equilibrium solid without range of homogeneity can be treated by the simple K_P method discussed in section III.B. A more detailed analysis of the gas phase is possible by a more sophisticated iteration method.[41] For this it is necessary to specify all homogeneous and heterogeneous equilibrium reactions. Therefore the kinds of condensed phases have to be known and must be fixed before the calculations.

To predict the kinds of formed (at T_{source}) and deposited (at T_{sink}) condensed phases one has to choose other methods:

1. The cooperative transport model[42,43] allows several steady states to be described during a transport process. It is possible to compute the sequence of deposition of several condensed phases without a homogeneity range.
2. The transport of solids with homogeneity range can be explained by the model of Krabbes *et al.*[44,45,74] This concept fails when the sequence of deposited phases is of interest.

Depending on the aspects of interest one has to decide between two computer-aided methods. If the magnitude of transport is not of interest the model of Piekarczyk[46,47] may be an alternative, too.

After the equilibrium calculations the interest is normally focused on the prediction of the transport rates of the condensed phases. For these calculations several concepts have been set up in the past. All models were developed assuming that the flux of the gaseous species proceeds by diffusion and net flux of the gas phase. Exceptions are the early model by Schäfer,[1,107,108] which was superseded by the concept of solubility in the gas phase,[134] and the model by Klosse and Ullersma,[187] which additionally takes into account the influence of convection on the transport rates.

For the calculation of the transport rates the equilibrium pressures have to be computed for the source and sink region. In most of the models these values are sufficient to calculate the fluxes. Exceptions are the models by Mandel[123] and Klosse:[187] additional information on the chemical equilibrium reactions (for example standard reaction enthalpy $\Delta_R H°_T$ in Mandel's or equilibrium constant $K_{P,t}$ in Klosse's) have to be given. Furthermore the diffusion has to be described by one mean diffusion coefficient (see models in sections III.C.1, III.C.2, III.C.4, and III.C.6−8) or by several binary diffusion coefficients

(III.C.3 and III.C.5). Using binary diffusion coefficients requires more computer time and does not automatically lead to more precise results.

The most convenient model is the concept of solubility by Schäfer[134] that works with one diffusion coefficient. It is used in the computer programs EPC,[37,38,157,176,177,189,190] GMIN,[192] and CVTrans.[191]

V. Chromium

A. Metal

Using iodine as transport agent (method after van Arkel and de Boer) chromium migrates via $CrI_{2,g}$ to the zone of higher temperature[237−239] (for more details see, e.g., refs 1, 34, and 35). This is due to the exothermic equilibrium eq V.1.

$$Cr_s + I_{2,g} = CrI_{2,g} \qquad (V.1)$$

On the other hand using HCl[240] or $CrCl_3$[241] as transport agents, chromium migrates in the opposite direction because of the positive reaction enthalpy.

B. Halides

The trivalent chromium halides CrX_3 (X = Cl, Br, I) can be transported by several transport agents, but the migration of the halide is accompanied by sublimation if the temperature is increased. Using halogens as transport agent ($CrCl_3/Cl_2$,[1,242] $CrBr_3/Br_2$,[35,58,243] and CrI_3/I_2[242,243]) it is possible to obtain crystals of the chromium trihalides. The migration is a result of the endothermic reactions eqs V.2 and V.3.

$$CrX_{3,s} = CrX_{3,g}\ (X = Cl, Br, I) \qquad (V.2)$$

$$CrX_{3,s} + {}^1/_2X_{2,g} = CrX_{4,g}\ (X = Cl, Br, I) \qquad (V.3)$$

From chlorine to iodine the participation of the sublimation equilibrium (eq V.2) (X = Cl, Br, I) becomes less important because of the diminished stability of $CrX_{3,g}$ with respect to the free energy of formation.

Besides sublimation another possibility exists to deposit $CrCl_3$ and $CrBr_3$ in the sink by heating in an appropriate temperature gradient without additional transport agent. $CrI_{3,s}$ decomposes completely into $CrI_{2,s}$ and $I_{2,g}$ under these conditions. The migration is a result of sublimation and chemical transport by $CrCl_{4,g}$[242] or $CrBr_{4,g}$,[58] which are formed by the partial disproportionation of a small amount of the halide ("auto transport").

$CrCl_3$ can also be transported by metal halides ($AlCl_3$,[115,244−246] $GaCl_3$,[245] or $NbCl_5$[245]) via gaseous metal complexes. In the case of $AlCl_3$ (500 → 400 °C) the migration is caused by the endothermic equilibrium:

$$CrCl_{3,s} + {}^3/_2Al_2Cl_{6,g} = CrAl_3Cl_{12,g} \qquad (V.4)$$

Of the known chromium(II) halides CrX_2, transport reactions are reported only for X = Cl. The migration of the chromium(II) halide to the lower temperature (350 → 250 °C) is mediated by $AlCl_3$,[246] whereas $GaCl_3$[154] effects a transport in both directions ($T > 380$ °C cold → hot, $T < 380$ °C hot → cold). Again, gaseous metal complexes are involved in the transport reaction.

$$CrCl_{2,s} + Al_2Cl_{6,g} = CrAl_2Cl_{8,g} \qquad (V.5)$$

$$CrCl_{2,s} + Ga_2Cl_{6,g} = CrGa_2Cl_{8,g} \qquad (T < 380\ °C) \qquad (V.6)$$

$$CrCl_{2,s} + 2GaCl_{3,g} = CrGa_2Cl_{8,g} \qquad (T > 380\ °C) \qquad (V.7)$$

C. Cr(III) Oxo Compounds

Generally chromium(III) oxo compounds can be transported in a temperature gradient from the hot to the cold zone with Cl_2 or HCl as transport agents. The transport rates are limited by the position of the respective volatilization equilibria. If the oxidation potential of the transport agent is reduced, the transport rates become smaller or even no migration is observed.

1. Cr_2O_3

Of the known chromium oxides only Cr_2O_3 can be transported in a temperature gradient. Hereto oxygen,[1] halogens (Cl_2[13,54,247−250] or Br_2[55,248]), halides ($HgCl_2$[54] or $TeCl_4$[35]), or mixtures of these ($CrBr_3/Br_2$[55] or CrI_3/I_2[56]) were used.

In the presence of oxygen Cr_2O_3 stays in equilibrium with the gaseous chromium(VI) oxide $CrO_{3,g}$.[1] The endothermic reaction (eq V.8) leads to the migration of Cr_2O_3 to the cooler zone of the ampule.

$$Cr_2O_{3,s} + {}^3/_2O_{2,g} = 2CrO_{3,g} \qquad (V.8)$$

In the case of Cl_2 as transport agent the migration of Cr_2O_3 is controlled by several endothermic reactions. Depending on the amount of chlorine present a change occurs in the transport mechanism.[13,54] For low concentrations of chlorine (and water from the wall of silica ampules) two equilibria determine the transport of $Cr_2O_{3,s}$.

$$Cr_2O_{3,s} + H_2O_g + 3Cl_{2,g} = 2CrO_2Cl_{2,g} + 2HCl_g \qquad (V.9)$$

$$Cr_2O_{3,s} + {}^1/_2O_{2,g} + 2Cl_{2,g} = 2CrO_2Cl_{2,g} \qquad (V.10)$$

Increasing the amount of Cl_2, the transport reaction changes to[13]

$$Cr_2O_{3,s} + {}^5/_2Cl_{2,g} = {}^3/_2CrO_2Cl_{2,g} + {}^1/_2CrCl_{4,g} \qquad (V.11)$$

Transport rates of up to 6.9 mg/h (1000 → 900 °C, $c(Cl_2) = 2.85$ mg/cm^3) were observed.[54]

When chromium is added to the transport system (decrease of the ratio $n°(Cl)/n°(Cr)$) the gas phase is reduced gradually and $CrCl_{3,g}$, $CrCl_{2,g}$, and $CrOCl_{2,g}$ become more important for the migration of Cr_2O_3 (for more details see ref 54).

Also, the use of bromine instead of chlorine as transport agent causes a transport of Cr_2O_3. In comparison to the Cr/O/Cl system the transport rates are smaller ($\dot{m}_{max}(Cr_2O_3) = 0.7$ mg/h, 1000 → 900 °C, $c(Br_2) = 17.15$ mg/cm^3).[55]

The transport experiments give strong evidence of the existence of chromium oxybromides. According to thermochemical model calculations based on estimated thermodynamic data of the chromium oxybromides in the bromine-containing transport system two equilibria control the migration of Cr_2O_3 (cf., eqs V.9 and V.10).[55]

$$Cr_2O_{3,s} + H_2O_g + 3Br_{2,g} = 2CrO_2Br_{2,g} + 2HBr_g \quad (V.12)$$

$$Cr_2O_{3,s} + {}^1/_2O_{2,g} + 2Br_{2,g} = 2CrO_2Br_{2,g} \quad (V.13)$$

With iodine a transport of Cr_2O_3 has not been observed.[56]

In comparison to halogen as transport agent mixtures of chromium(III) halide and halogen (CrX_3/X_2, X = Br,[55] I[56]) yield higher transport rates. The partial pressure of oxygen is lowered. By adding CrX_3 the chromium oxyhalide $CrOX_{2,g}$ becomes an important gaseous species for the transport of Cr_2O_3, and $CrX_{4,g}$ has to be considered as transport agent.

$$Cr_2O_{3,s} + 3CrBr_{4,g} = 3CrOBr_{2,g} + 2CrBr_{3,g} \quad (V.14)$$

$$Cr_2O_{3,s} + 2CrI_{4,g} = 3CrOI_{2,g} + CrI_{2,g} \quad (V.15)$$

Concluding from experimental data it was possible to fix the estimated values of the enthalpies of formation for $CrOX_{2,g}$ (X = Br, I) and $CrO_2Br_{2,g}$ more precisely by thermochemical model calculations.[55,56]

2. Oxospinels

It is of general interest to grow large single crystals of chromium oxo-, thio-, and selenospinels MCr_2X_4 (M = Fe, Mn, Ni, Co, Zn, Cd, Hg, Cu; X = O, S, Se; see Table 1), because of their magnetic, electrical, and optical properties. The physical properties of these substances strongly depend on their composition (stoichiometric or nonstoichiometric) and on doping. Transport reactions are widely used to grow such crystals and to control their physical properties by varying the composition of the gas phase.

According to Peshev *et al.*[252] $CoCr_2O_4$ and $NiCr_2O_4$ migrate via CrO_2Cl_2, $CoCl_2$, and $NiCl_2$, respectively using Cl_2 as transport agent. The gas-phase composition was calculated (also for $ZnCr_2O_4/Cl_2$[253]). Transport rates up to $\dot{n} = 9.9 \times 10^{-5}$ mol/m^2 s ($CoCr_2O_4$, 1050 → 950 °C) and 6.6×10^{-5} mol/m^2 s ($NiCr_2O_4$, 1030 → 970 °C) were observed.

$$MCr_2O_{4,s} + 3Cl_{2,g} = CrO_2Cl_{2,g} + MCl_{2,g} \ (M = Co, Ni) \quad (V.16)$$

Several oxospinels ($MnCr_2O_4$,[251] $CoCr_2O_4$,[251] and $NiCr_2O_4$[251]) migrate with HCl as transport agent, too, but no thermochemical calculations were performed for these systems.

Many transport systems (e.g., $CoCr_2O_4/Cl_2$,[252] $NiCr_2O_4/Cl_2$,[252] $ZnCr_2O_4/Cl_2$,[253] $CdCr_2S_4/CrCl_3$,[254] and $HgCr_2Se_4/CrCl_3$[254]) have been analyzed by means of thermochemical calculations based on different models of chemical vapor transport and the results have been compared with the experimental data. These papers mainly deal with the volatilization of the solid in the gas phase and the relationships between equilibrium composition of the solid and the gas phase. Transport rates were not derived from these calculations. These thermodynamic analyses often allow a better choice of transport agent and temperature gradients.

3. Phosphates and Sulfates

α-$CrPO_4$ can be crystallized in a temperature gradient using Cl_2 as transport agent.[255] The observed transport rates are low ($\dot{m}$ < 0.1 mg/d, 1100 → 1000 °C, $c(Cl_2) = 2.90$ mg/cm^3).

Crystals of rhombohedral anhydrous chromium(III) sulfate can be grown in the less hot zone of a closed silica ampule by means of chemical transport using Cl_2 or HCl as transport agents.[256,257] Thermochemical calculations show that the transport of the sulfate is caused by the flux of CrO_2Cl_2, SO_3, SO_2, and O_2 from the hot to the cold zone.[257]

$$Cr_2(SO_4)_{3,s} + 2Cl_{2,g} = 2CrO_2Cl_{2,g} + (2 - x)SO_{3,g} + (1 + x)SO_{2,g} + (x/2)O_{2,g} \quad (V.17)$$

$(0 \le x \le 2,\ x = 0$ for $\bar{T} < 520$ °C and $x = 2$ for $\bar{T} > 780$ °C)

$$Cr_2(SO_4)_{3,s} + 4HCl_g = 2CrO_2Cl_{2,g} + 3SO_{2,g} + 2H_2O_g \quad (V.18)$$

4. CrOCl

In a temperature gradient CrOCl migrates to the zone of lower temperature even if no transport agent is added.[1,13] This is a result of several consecutive heterogeneous and homogeneous equilibria.[13]

CrOCl can be transported from hot to cold using Cl_2 as transport agent.[13,258] According to Nocker and Gruehn[13] the migration of CrOCl in a temperature gradient (600 → 500 °C) in the presence of chlorine is the result of the endothermic reaction

$$2CrOCl_s + 2Cl_{2,g} = CrO_2Cl_{2,g} + CrCl_{4,g} \quad (V.19)$$

With the use of the transport balance,[9] it was possible to observe several consecutive stationary depositions, and nonstationary changes in the gas phase could be recognized.[13]

It is also possible to crystallize CrOCl by using HCl[13] (eq V.20) or $HgCl_2$[13] as transport agents.

$$CrOCl_s + 2HCl_g = CrCl_{3,g} + H_2O_g \quad (V.20)$$

5. Other Compounds

Chromium niobate $CrNbO_4$ and chromium tantalate $CrTaO_4$ can be transported using Cl_2 or HCl as transport agents.[251] It is also possible to obtain crystals of $CrNbO_4$ with a mixture of Cl_2 and $NbCl_5$ as transport agent (980 → 860 °C).[247,259]

$Mn_3Cr_2Ge_3O_{12}$ (MCGG) crystallizes in a temperature gradient (950 → 880 °C) using Cl_2,[260] I_2,[260] or a mixture of X/Cl_2 (X = C, S, Te)[260] as transport agents.

$$Mn_3Cr_2Ge_3O_{12,s} + 8Cl_{2,g} = 3MnCl_{2,g} + 2CrO_2Cl_{2,g} + 3GeCl_{2,g} + 4O_{2,g} \quad (V.21)$$

$$Mn_3Cr_2Ge_3O_{12,s} + 9I_{2,g} = 3MnI_{2,g} + 2CrI_{3,g} + 3GeI_{2,g} + 6O_{2,g} \quad (V.22)$$

Table 1. Chemical Transport of Chromium and Chromium Compounds[a]

substance	transport agent	ref(s)
Cr	I_2 (−)	237−239
	HCl (+)	240
	$CrCl_3$ (+)	241
CrB	X_2 (X = Cl, Br, I) (+)	263
CrB_2	X_2 (X = Cl, Br, I) (+)	263
Cr_3Si	X_2 (X = Cl, Br) (+)	263,264
	I_2 (−)	263,264
Cr_5Si_3	X_2 (X = Cl, Br) (+)	264
	I_2 (−)	264
CrSi	Br_2 (+)	264
	I_2 (-)	264
$CrSi_2$	Cl_2 (+)	264−266
	Br_2 (+)	264−266
	I_2 (−)	264,265
CrP	I_2 (+)	57
CrAs	I_2 (+)	267
Cr_2O_3	O_2 (+)	1
	Cl_2 (+)	13,54,247−250
	Br_2 (+)	55,248
	$CrBr_3/Br_2$ (+)	55
	CrI_3/I_2 (+)	56
	$HgCl_2$ (+)	54
$Fe_{2-y}Cr_yO_3$	Cl_2 (+)	261
	$FeCl_3$ (+)	261
	$TeCl_4$ (+)	262
$MnCr_2O_4$	Cl_2 (+)	251
	HCl (+)	251
$CoCr_2O_4$	Cl_2 (+)	251,252
	HCl (+)	251
$NiCr_2O_4$	Cl_2 (+)	251,252
	HCl (+)	251
$M(Fe,Cr)_2O_4$ (M = Mn, Ni)	Cl_2 (+)	251
	HCl (+)	251
$ZnCr_2O_4$	Cl_2 (+)	253
$CrNbO_4$	Cl_2 (+)	251
	HCl (+)	251
	$Cl_2/NbCl_5$ (+)	247
$CrTaO_4$	Cl_2 (+)	251
	HCl (+)	251
$Mn_3Cr_2Ge_3O_{12}$	X_2 (X = Cl, I) (+)	260
	X/Cl_2 (X = C, S, Te) (+)	260
$Cr_3B_7O_{13}Br$	Br_2 (+)	312,313
α-$CrPO_4$	Cl_2 (+)	255
$Cr_3(PO_4)_2$	I_2 (+)	308
$Cr_2P_2O_7$	I_2 (+)	309
	NH_4Cl (+)	309
$Cr_7(PO_4)_6$	I_2 (+)	310
$Cr_6(P_2O_7)_4$	I_2 (+)	311
$Cr_2(SO_4)_3$	Cl_2 (+)	257
	HCl (+)	256,257
CrS	$AlCl_3$ (+)	268,269
Cr_7S_8	$AlCl_3$ (+)	240,268,269
Cr_5S_6	$AlCl_3$ (+)	240,268,269
Cr_3S_4	$AlCl_3$ (+)	240,268−270
	$AlCl_3/CrCl_3$ (+)	270
Cr_2S_3	Br_2 (+)	30
	I_2 (+)	271
	S_2 (+)	272
	HCl (+)	269,275
	$AlCl_3$ (+)	240,268,269,274
	$CrCl_3$ (+)	240,274,275
$MnCr_2S_4$	$AlCl_3$ (+)	240,268,270
$FeCr_2S_4$	Cl_2 (+)	278,279
	HCl (+)	286−288
	$CrCl_3$ (+)	289−292
	Cl_2/HCl (+)	279,294
	$HCl/CrCl_3$ (+)	240,288,291
$CoCr_2S_4$	$CrCl_3$ (+)	289
	Cl_2/HCl (+)	294
	$HCl/CrCl_3$ (+)	240
$NiCr_2S_4$ ($Ni_{1-x}Cr_{2+x}S_4$)	$AlCl_3$ (+)	269,270
	$AlCl_3/CrCl_3$ (+)	240,270
$CuCr_2S_4$	Cl_2 (+)	287
$ZnCr_2S_4$	$AlCl_3$ (+)	240,268,270
$CdCr_2S_4$	Cl_2 (+)	240,280−284
	I_2 (+)	283,285
	$AlCl_3$ (+)	285
	$CrCl_3$ (+)	254,283,293
	Cl_2/HCl (+)	294
$HgCr_2S_4$	Cl_2 (+)	275
$Fe_{1-x}Cu_xCr_2S_4$	Cl_2 (+)	287
$(M,Co)Cr_2S_4$ (M = Mn, Zn, Cd)	$AlCl_3$ (+)	240,269,270
Cr_7Se_8	$AlCl_3$ (+)	240,269
Cr_2Se_3	$AlCl_3$ (+)	240,269,274
	$CrCl_3$ (+)	274
$Cr_2S_{3-x}Se_x$	$AlCl_3$ (+)	274
	$CrCl_3$ (+)	274
$ZnCr_2Se_4$	$AlCl_3$ (+)	240,269,270
$CdCr_2Se_4$	HCl/Cl_2 (+)	294
	$AlCl_3$ (+)	240,269,270
	$CrCl_3$ (+)	296
	$CdCl_2$ (+)	295
$CuCr_2Se_4$	$AlCl_3$ (+)	240,269,270
	I_2 (+)	297,298
$HgCr_2Se_4$	Cl_2 (+)	299,301
	Br_2 (+)	299
	$AlCl_3$ (+)	240,269,270
	$CrCl_3$ (+)	254,282,299−303
	$HgCl_2$ (+)	245,299,301
	$HgBr_2$ (+)	299
	CrO_2Cl_2 (+)	299,301
	$AlCl_3/Cl_2$ (+)	302
$Cu_xGa_{1-x}Cr_2Se_4$	$CrCl_3$ (+)	304
$Cu_xHg_{1-x}Cr_2Se_4$	$AlCl_3$ (+)	305
$CdCr_2(S_{1-x}Se_x)_4$	$I_2/AlCl_3$ (+)	285
$ZnCr_2(S_{1-x}Se_x)_4$	$I_2/AlCl_3$ (+)	307
$Cd_{1-x}M_xCr_2Se_4$ (M = In, Al, Ag, Cu)	$CdCl_2$ (+)	306
$FeCr_2S_{4-x}Se_x$	HCl/Cl_2 (+)	294
CrTe	I_2 (−)	1
$CrCl_2$	$AlCl_3$ (+)	246
	$GaCl_3$ (−/+)	154
$CrCl_3$	auto transport (+)	242
	Cl_2 (+)	1,242
	$AlCl_3$ (+)	115,244−246
	$GaCl_3$ (+)	245
	$NbCl_5$ (+)	245
$CrBr_3$	auto transport (+)	58
	Br_2 (+)	35,58,243
CrI_3	I_2 (+)	242,243
CrOCl	auto transport (+)	1,13
	Cl_2 (+)	13,258
	HCl (+)	13
	$HgCl_2$ (+)	13

[a] Key: (+) $T_2 \rightarrow T_1$ "endothermic transport", (−) $T_1 \rightarrow T_2$ "exothermic transport" ($T_2 > T_1$).

$$Mn_3Cr_2Ge_3O_{12,s} + 4XCl_{4,g} = 3MnCl_{2,g} + 2CrO_2Cl_{2,g} + 3GeCl_{2,g} + 4XO_{2,g} \quad (V.23)$$

$$(X = C, S, Te)$$

In our opinion the given transport equations are not a satisfactory explanation of the transport behavior of MCGG. It seems to be more obvious that the gaseous species $GeCl_4$ (instead of $GeCl_2$), SO_2, and SO_3 (instead of SCl_4) are—due to their stability—of more importance in the transport systems Mn/Cr/Ge/O/X/Cl (X = C, S, Te).

The nonstoichiometric ternary compound $Fe_{2-y}Cr_yO_3$ migrates in a temperature gradient ($T_2 \rightarrow T_1$) using Cl_2,[261] $FeCl_3$ ($\dot{m}$ = 1.5−9 mg/h, 1070 → 770 °C)[261] or $TeCl_4$[262] as transport agents. For the transport systems $Fe_{2-y}Cr_yO_3/FeCl_3$[261] and $Fe_{2-y}Cr_yO_3/TeCl_4$[262] the compositions of the equilibrium solids were calculated.

D. Intermetallic Compounds

1. Borides, Silicides, Phosphides, and Arsenides

The chromium borides CrB and CrB_2 migrate from hot to cold, if halogens (Cl_2, Br_2, or I_2) are added as transport agent.[263]

Preparation of single crystals of Cr_3Si, Cr_5Si_3, CrSi,[264] and $CrSi_2$[264−266] is possible by several transport reactions using halogens (Cl_2, Br_2, or I_2) as transport agents.

Krausze *et al.*[265] report the transport behavior of $CrSi_2$ (TA Cl_2, Br_2, I_2). Detailed experimental results ($\dot{m}_{max}(CrSi_2) = 1.8$ mg/h, 1100 → 1000 °C, TA Br_2) and a transport model based on thermochemical calculations are given. According to these, $CrSi_2$ migrates from hot to cold in the chlorine- and bromine-containing system.

$$CrSi_{2,s} + 8SiCl_{4,g} = CrCl_{2,g} + 10SiCl_{3,g} \qquad (V.24)$$

$$CrSi_{2,s} + 3SiBr_{4,g} = CrBr_{2,g} + 5SiBr_{2,g} \qquad (V.25)$$

While using iodine as transport agent an opposite transport direction is found.

$$CrSi_{2,s} + 10I_g = CrI_{2,g} + 2SiI_{4,g} \qquad (V.26)$$

The migration of the chromium rich silicides Cr_3Si, Cr_5Si_3, and CrSi shows a behavior similar to $CrSi_2$. While chlorine and bromine cause a transport from hot to cold, iodine effects a transport in the reverse direction. A detailed discussion of the transport (transport rates, composition of the gas phase, and the subsequent transport behavior of the solids) in the system Cr/Si ($n°(Cr)/n°(Si) > 1$) has been published.[264] The incongruent dissolution of the silicides in the gas phase leads to different equilibrium solids. In spite of this, the migration of the chromium silicides ($\dot{m}_{exp}(CrSi_n) = 1-10$ mg/h) can be described by the following equation:[264]

$$CrSi_{n,s} + (1{+}2n)X_{2,g} = CrX_{2,g} + nSiX_{4,g} \quad (X = Cl, Br) \quad (n = 0.33, 0.375, 1) \quad (V.27)$$

With iodine the transport mechanism becomes more complicated.[264]

Chromium monophosphide CrP is deposited at the lower temperature using iodine as transport agent. Transport rates up to 16.8 mg/h were observed (e.g., 1050 → 950 °C, $c(I_2) = 7.61$ mg/cm^3).[57] According to thermochemical calculations CrP is dissolved in the gas phase by formation of $CrI_{2,g}$, $Cr_2I_{4,g}$, $P_{2,g}$, and $P_{4,g}$, while $PI_{3,g}$, $P_2I_{4,g}$, HI_g, and $I_{2,g}$ have to be considered as effective transport agents. Depending on $c(I_2)$ $CrI_{2,s}$ is deposited in addition to CrP in the sink region.

Selte *et al.*[267] obtained crystals of CrAs by means of iodine.

2. Chalcogenides

The synthesis of chromium sulfides (CrS,[268,269] Cr_7S_8,[240,268,269] Cr_5S_6,[240,268,269] Cr_3S_4,[240,268−270] and Cr_2S_3[30,240,268,269,271−275]), chromium selenides (Cr_7Se_8[240,269] and Cr_2Se_3,[240,269,274]) and chromium telluride (CrTe[1]) is performed in a temperature gradient ($T_2 \rightarrow T_1$, $T_2 > T_1$) with several transport agents. It is also possible to obtain mixed chalcogenides $Cr_2S_{3-x}Se_x$.[274]

Following Lutz *et al.*,[240,268,269] the chromium sulfides can be transported with $AlCl_3$ or $CrCl_3$ as transport agents. The transport equilibria for $AlCl_3$-containing systems as published by Lutz *et al.*[268,269] seem to be an insufficient explanation for the observed transport behavior.[240]

Cr_2S_3 crystals can also be grown in a temperature gradient (1020 → 890 °C) in the presence of excess sulfur as transport agent.[272] Up to now it is unknown by which gaseous species the migration of the chromium sulfide is mediated. If Br_2[30] or I_2[271] are added to the transport system, a transport effect is observed, too.

After Schäfer, CrTe[1] transports in the presence of iodine according to the endothermic reaction:

$$CrTe_s + I_{2,g} = CrI_{2,g} + {}^1/_2Te_{2,g} \qquad (V.28)$$

E. Other Compounds

1. Chalcogenide Spinels

The reviews of von Philipsborn[276] and Gibart *et al.*[277] cover crystal growth and crystallographic and chemical characterization of several thio- and selenospinels.

a. Thiospinels. Due to their reduced stability compared with the oxospinels only a few thiospinels can be transported with oxidizing transport agents ($FeCr_2S_4/Cl_2$,[278,279] $CdCr_2S_4/Cl_2$,[280−284] and $HgCr_2S_4/Cl_2$[275]). Considerable yields were found, when I_2 ($CdCr_2S_4$[283,285]), HCl ($FeCr_2S_4$,[286−288] $CuCr_2S_4$,[287] and $Fe_{1-x}Cu_xCr_2S_4$[287]), $CrCl_3$ ($FeCr_2S_4$,[289−292] $CoCr_2S_4$,[289] and $CdCr_2S_4$[254,283,293]), $AlCl_3$ ($NiCr_2S_4$[269,270] and $CdCr_2S_4$[285]) or mixtures of these were applied (Cl_2/HCl,[278,279,294] HCl/$CrCl_3$,[240,288,291] or $AlCl_3/CrCl_3$[240,270]). The results of the transport experiments were verified by thermochemical analysis in only a few cases. The composition of the gas phases were calculated in the following transport systems: $FeCr_2S_4/Cl_2$,[279] $FeCr_2S_4/HCl/Cl_2$,[279,294] $MCr_2S_4/HCl/Cl_2$ (M = Co, Cd),[294] $CdCr_2S_4/X_2$ (X = Cl, I),[283] $CdCr_2S_4/CrCl_3$,[283] and $MCr_2S_4/CrCl_3$ (M = Cd, Hg).[254]

Barraclough and Meyer[283] investigated the transport systems $CdCr_2S_4/X_2$ (X = Cl, I) and $CdCr_2S_4/CrCl_3$ ($\dot{n} = 10^{-4}$ mol/d, 950 → 900 °C, $c(CrCl_3) = 1.00$ mg/cm^3) and propose a transport reaction for the migration of the thiospinel:

$$CdCr_2S_{4,s} + 4X_{2,g} = CdX_{2,g} + 2CrX_{3,g} + 2S_{2,g} \quad (X = Cl, I) \quad (V.29)$$

b. Selenospinels. In the past, there was a great interest in growing crystals of selenospinels ($ZnCr_2Se_4$,[240,269,270] $CdCr_2Se_4$,[240,269,270,294−296] $CuCr_2Se_4$,[240,269,270,297,298] and $HgCr_2Se_4$[245,254,269,270,282,299−303]). Therefore, various transport agents were examined for their efficiency for the transport of several spinels to influence the physical properties of the crystals. The authors found that the selenospinels migrate under conditions similar to these of the thiospinels. However, the temperatures of transport are considerably lower than in the thio- or oxospinel systems.

Gibart[302] investigated the transport system $HgCr_2Se_4/AlCl_3/Cl_2$. The chromium part of the ferromagnetic semiconductor transports via the gaseous complexes $CrAl_2Cl_8$ and $CrAl_3Cl_{12}$, while mercury migrates as Hg and selenium as a Se_2/Se_6 mixture through the gas phase. The composition of the equilibrium gas phase is also given by this author.[302]

Wehmeier[295] proposes for the transport of $CdCr_2Se_4$ with $CdCl_2$ as transport agent (800 → 700 °C).

$$CdCr_2Se_{4,s} + 3CdCl_{2,g} = 4Cd_g + 2Se_{2,g} + CrCl_{3,g} \qquad (V.30)$$

It is also possible to obtain mixed thio-, seleno-, and thioselenospinels by chemical transport reactions ($(M,Co)Cr_2S_4$ (M = Mn, Zn, Cd),[240,269,270] $Cu_xGa_{1-x}Cr_2Se_4$,[304] $Cu_xHg_{1-x}Cr_2Se_4$,[305] $Cd_{1-x}M_xCr_2Se_4$ (M = In, Al, Ag, Cu),[306] $CdCr_2(S_{1-x}Se_x)_4$,[285] $ZnCr_2(S_{1-x}Se_x)_4$,[307] and $FeCr_2(S_{1-x}Se_x)_4$[294]). In these papers the composition and physical properties of these crystals were investigated. The experimental data of these transport experiments are given without thermochemical calculations.

2. Cr(II) and Cr(II,III) Compounds

The chromium phosphates $Cr_3(PO_4)_2$,[308] $Cr_2P_2O_7$,[309] $Cr_7(PO_4)_6$,[310] and $Cr_6(P_2O_7)_4$[311] can be transported with iodine as transport agent. On the basis of the estimated data for $Cr_2P_2O_7$, it seems to be possible that the migration of the phosphate proceeds via $CrI_{2,g}$ and $P_4O_{6,g}$ if phosphorus or chromium monophosphide is added to the system:[309]

$$Cr_2P_2O_{7,s} + 2I_{2,g} + {}^2/_3P_{2,g} = 2CrI_{2,g} + {}^7/_6P_4O_{6,g} \qquad (V.31)$$

There are no thermochemical data for $Cr_3(PO_4)_2$, $Cr_7(PO_4)_6$, and $Cr_6(P_2O_7)_4$ available. It is therefore not possible to provide transport equilibria for these compounds.

Crystals of the chromium boracite $Cr_3B_7O_{13}Br$ can be transported using Br_2 as the transport agent.[312,313]

VI. Molybdenum

A. Metal

For a general survey of chemical transport reactions leading to the migration of Mo from T_2 to T_1 see Table 2. Most of the transport agents (e.g., Cl_2,[314−316] or I_2/H_2O[317]) effect the migration of the metal from the zone of lower temperature to the one of higher temperature ($T_1 \rightarrow T_2$, $T_1 < T_2$, exothermic transport reaction).

For instance, Mo migrates, by using iodine as transport agent, only if water is present in the transport system. Because of the instability of the molybdenum iodides, particularly the tetraiodide $MoI_{4,g}$, the transport has to proceed via $MoO_2I_{2,g}$ according to the exothermic equilibrium (VI.1) (for details see ref 317):

$$Mo_s + 2H_2O_g + 3I_{2,g} = MoO_2I_{2,g} + 4HI_g \qquad (VI.1)$$

The observed transport rates are less than 2.7 mg/h (1050 → 1150 °C, $c(I_2) = 3.30$ mg/cm^3).

To our knowledge there are only a few systems in which Mo migrates from the higher to the lower temperature ($T_2 \rightarrow T_1$, $T_2 > T_1$) according to an endothermic reaction, namely: Mo/H_2O,[318,319] $Mo/HgBr_2$,[10] and $Mo/SbBr_3$.[320]

Molybdenum migrates from the higher to the lower temperature region with $HgBr_2$ as a transport agent. Together with Mo we observed $MoBr_2$ and MoO_2 as additional equilibrium solids in the sink region. Both solids are formed by the reaction of the elementary Mo with the transport agent or with oxygen-containing impurities or H_2O out of the silica wall of the ampule.[49] With the occurrence of these equilibrium solids an additional steady-state of deposition is developed prior to the migration of Mo (Figure 4). In this first steady-state $MoBr_2$ and MoO_2 migrate simultaneously by two independent transport reactions:

$$MoBr_{2,s} + HgBr_{2,g} = MoBr_{4,g} + Hg_g \qquad (VI.2)$$

$$MoO_{2,s} + HgBr_{2,g} = MoO_2Br_{2,g} + Hg_g \qquad (VI.3)$$

The deposition of $MoBr_2$ and MoO_2 is followed by the migration of Mo according to the endothermic reaction:

$$Mo_s + 2HgBr_{2,g} = MoBr_{4,g} + 2Hg_g \qquad (VI.4)$$

When there is oxygen present in the transport system the deposition rates of the metal are drastically reduced. The contamination of the system, by oxygen coming from impurities or water from the wall of the silica ampule, can be easily simulated by introducing MoO_2 into the system. This leads to a smaller $HgBr_2$ partial pressure (eq VI.3) and, according to the transport reaction (eq VI.4), to smaller deposition rates of the metal. The maximum transport rate ($\dot{m}_{max} = 41.0$ mg/h, 1000 → 900 °C, $c(HgBr_2) = 8.65$ mg/cm^3) decreases to values less than 5 mg/h (1020 → 960 °C) if MoO_2 is present as an equilibrium solid.

Thus best agreements between calculations and experimental data were obtained assuming the presence of oxygen in the starting materials. According to our model calculations, the gas phase in the system $Mo/H_2O/HgBr_2$ consists primarily of Hg, MoO_2Br_2, HBr, $HgBr_2$, and $MoBr_4$. For more details see ref 10.

The use of $HgCl_2$ as transport agent[190] leads to the formation of $MoCl_2$ as an additional solid at T_2. Due to the higher stability of $MoCl_2$, in comparison to $MoBr_2$ (see ref 321), the deposition rate of Mo is reduced to zero. Only the deposition of $MoCl_2$ (and MoO_2) at T_1 is observed.

With $SbBr_3$ as transport agent, molybdenum can be transported from hot to cold, too.[320] The deposition rates are smaller than those using $HgBr_2$ as transport agent ($\dot{m}_{max} = 16.0$ mg/h, 1000 → 900 °C, $c(SbBr_3) = 7.21$ mg/cm^3). MoO_2Br_2 is the most important molybdenum containing gaseous species (see eq VI.5):

$$Mo_s + 2H_2O_g + 2SbBr_{3,g} = MoO_2Br_{2,g} + 4HBr_g + {}^1/_2Sb_{4,g} \qquad (VI.5)$$

Together with molybdenum, MoO_2 and Sb are observed at T_1 as additional equilibrium solids.

Mo/W-mixed crystals can be prepared with $HgBr_2$ as transport agent (e.g., $\dot{m} = 3.6$ mg/h, 1050 → 950

Table 2. Chemical Transport of Molybdenum and Molybdenum Compounds[a]

substance	transport agent	ref(s)	substance	transport agent	ref(s)
Mo	Cl_2 (−)	314−316	$Cu_3Mo_2O_9$	X_2 (X = Cl, Br) (+)	100
	H_2O/H_2 (+)	318,319		HCl (+)	100
	I_2/H_2O (−)	317		$TeCl_4$ (+)	100
	$HgBr_2$ (+)	10	$MMoO_4$ (M = Mg, Co, Ni)	Cl_2 (+)	251
	$SbBr_3$ (+)	320		HCl (+)	251
Mo/W	$HgBr_2$ (+)	155	$M_2Mo_3O_8$ (M = Mn, Fe, Co, Ni)	$TeCl_4$ (+)	353,354
Mo_3P	$HgBr_2$ (+)	357	$Mo(PO_3)_3$	I_2 (+)	355,356
Mo_4P_3	I_2 (+)	356		NH_4I (+)	356
	$HgBr_2$ (+)	357	MoP_2O_7	I_2 (+)	356
MoP	I_2 (+)	356		$HgBr_2$ (+)	356
	$HgBr_2$ (+)	357	$MoPO_5$	I_2 (+)	356
Mo_5As_4	X_2 (X = Cl, Br) (+)	358,359	$Mo_4P_6O_{25}$	I_2 (+)	356
	I_2 (+)	358−361	$Mo_2P_4O_{15}$	I_2 (+)	356
Mo_2As_3	X_2 (X = Cl, Br) (+)	358,359		HgX_2 (X = Cl, Br) (+)	356
	I_2 (+)	358−361	MoS_2	S_2 (+)	272,362
$MoAs_2$	X_2 (X = Cl, Br) (+)	358,359		Cl_2 (+)	1
	I_2 (+)	358−361		Br_2 (+)	362−364
Mo_3Sb_7	I_2 (+)	360,361		I_2 (+)	317
MoO_2	I_2 or I_2/H_2O (+)	34,317,329−333		HBr (+)	363
	H_2O (+)	317,329		NH_4Br (+)	363
	$TeCl_4$ (+)	334−340		MBr_2 (M = Ge, Sn) (+)	363
	$TeBr_4$ (+)	335,337	Mo_2S_3	X_2 (X = Cl, Br) (+)	363
	TeI_4 (+)	338		HBr (+)	363
	$HgCl_2$ (+)	59		NH_4Br (+)	363
	$HgBr_2$ (+)	10,60		MBr_2 (M = Ge, Sn) (+)	363
	HgI_2 (+)	190	$PbMo_6S_8$	$PbCl_2$ (+)	365
Mo_4O_{11}	I_2 (+)	341−343	$MoSe_2$	Se (+)	362,366−368
	$TeCl_4$ (+)	18,336,341−345		Br_2 (+)	1,362,364,367,368,371
	$HgCl_2$ (+)	59		I_2 (+)	1,367,368
	$HgBr_2$ (+)	60		XCl_4 (X = Se, Te) (+)	367,368
	HgI_2 (+)	190	$Mo_{1-x}W_xSe_2$	Br_2 (+)	369
Mo_8O_{23}	$TeCl_4$ (+)	336	$MoTe_2$	Br_2 (+)	1,362,370−373
Mo_9O_{26}	$TeCl_4$ (+)	336		I_2 (+)	374
MoO_3	Cl_2 (+)	346		$TeCl_4$ (+)	375
	H_2O (+)	347,348	$Mo_{1-x}W_xTe_2$	Br_2 (+)	370
	HCl (+)	349	$MoCl_2$	autotransport (+)	322
	$TeCl_4$ (+)	336	$MoCl_3$	autotransport (+)	147,322,323
	$HgCl_2$ (+)	346		$AlCl_3$ (+)	245
$V_{1-x}Mo_xO_2$	Cl_2 (+)	350	$MoBr_2$	Br_2 (+)	35,324
	$TeCl_4$ (+)	351		$HgBr_2$ (+)	10
$MnMoO_4$	Cl_2 (+)	99,251	$MoBr_3$	Br_2 (+)	324
	HCl (+)	99,251	$MoOCl_2$	$MoCl_5$ (+)	323
	XCl_4 (X = Se, Te) (+)	99	$MoOBr_3$	Br_2 (+)	325
$Mn_2Mo_3O_8$	I_2 (+)	99	MoSCl	Cl_2 (+)	363
	HX (X = Cl, I) (+)	99	MoSBr	Br_2 (+)	363
	XCl_4 (X = Se, Te) (+)	99	$Te_4(MoOCl_4)_2$	autotransport (+)	326
$ZnMoO_4$	Cl_2 (+)	352	$Se_4(MoOCl_4)_2$	autotransport (+)	327
$Zn_2Mo_3O_8$	HX (X = Cl, Br) (+)	352	$[Te_{15}X_4]_n[MoOX_4]_{2n}$ (X = Cl, Br)	autotransport (+)	328
	I_2 (+)	352			
$CuMoO_4$	X_2 (X = Cl, Br) (+)	100			
	HCl (+)	100			
	$TeCl_4$ (+)	100			

[a] Key: (+) $T_2 \rightarrow T_1$ "endothermic transport", (−) $T_1 \rightarrow T_2$ "exothermic transport" ($T_2 > T_1$).

°C).[155] The composition of the crystals varies over a broad range.

B. Halides and Oxyhalides

The crystallization of some of the molybdenum halides by chemical transport reactions is quite facile. The migration caused by chemical transport is often accompanied by sublimation of the halide. In most of the cases the transport is merely used for the purification of the compound. The transport reactions proposed by different authors represent thermodynamically meaningful transport equilibria but are not the result of thermochemical model calculations.

$MoCl_2$ migrates without an additional transport agent.[322] The migration can be described by the endotherm reaction of $MoCl_2$ with gaseous $MoCl_4$, which is formed by the partial disproportionation of $MoCl_2$ ("auto transport").

$$MoCl_{2,s} + MoCl_{4,g} = 2MoCl_{3,g} \qquad (VI.6)$$

$MoCl_3$ migrates in a similar way:[147,322,323]

$$MoCl_{3,s} + MoCl_{5,g} = 2MoCl_{4,g} \qquad (VI.7)$$

It is also possible to obtain crystals of $MoCl_3$ with $AlCl_3$ as transport agent (400 → 350 °C):[245]

$$MoCl_{3,s} + {}^{3}/_{2}Al_2Cl_{6,g} = MoAl_3Cl_{12,g} \qquad (VI.8)$$

$MoBr_2$[35,324] (1100 → 900 °C) and $MoBr_3$[324] (450 → 350 °C) can be crystallized with bromine as transport agent. In both cases the halide migrates via $MoBr_{4,g}$:

$$MoBr_{2,s} + Br_{2,g} = MoBr_{4,g} \qquad (VI.9)$$

$$MoBr_{3,s} + {}^{1}/_{2}Br_{2,g} = MoBr_{4,g} \qquad (V.10)$$

$MoOCl_2$,[323] $MoOBr_3$,[325] $Te_4(MoOCl_4)_2$,[326] $Se_4(MoOCl_4)_2$,[327] and $[Te_{15}X_4][MoOX_4]_2$ (X = Cl, Br)[328] can also be transported. The migration from hot to cold is caused by chemical transport and sublimation ("auto transport").

C. Oxides

1. Dioxide

Only endothermic transport reactions ($T_2 \rightarrow T_1$, $T_2 > T_1$) are reported for MoO_2. With iodine as transport agent MoO_2 migrates via gaseous MoO_2I_2.[34,317,329−333]

$$MoO_{2,s} + I_{2,g} = MoO_2I_{2,g} \qquad (VI.11)$$

The transport rate of MoO_2 is small ($\dot{m}_{exp} \approx 0.2$ mg/h, 730 → 650 °C, $c(I_2) = 1.61$ mg/cm^3).

When H_2O is used as transport agent,[317,329] there is a transport effect, too. In this case MoO_2 migrates from the source to the sink via $MoO_2(OH)_2$ (H_2MoO_4).

$$MoO_{2,s} + 2H_2O_g = MoO_2(OH)_{2,g} + H_{2,g} \qquad (VI.12)$$

The transport rates are small, too ($\dot{m}_{exp} \approx 0.7$ mg/h, 1000 → 900 °C, $c(H_2O) = 0.59$ mg/cm^3).[317]

Experimental results and model calculations are reported by Schäfer *et al.*[317] and Ben-Dor and Conroy.[329]

Very effective transport agents for the transport of molybdenum dioxide are the tellurium tetrahalides TeX_4 (X = Cl, Br, I)[334−340] with $TeX_{2,g}$ being the active transport agent. Transport rates up to 50 mg/h (X = Br) and 14 mg/h (X = Cl) were observed:

$$MoO_{2,s} + TeX_{2,g} = MoO_2X_{2,g} + {}^{1}/_{2}Te_{2,g} \quad (X = Br, I) \qquad (VI.13)$$

Mercury dihalides HgX_2 (X = Cl, Br, I) are transport agents of great effectiveness.

By using $HgCl_2$, deposition rates up to 58 mg/h (620 → 540 °C, $c(HgCl_{2,g}) = 1.26$ mg/cm^3) were observed.[59] Experimental results and data based on thermochemical model calculations are in good agreement, when a smaller diffusion coefficient ($D_o = 0.025$ cm^2/s instead of 0.1 cm^2/s) [1,335] is applied.[59]

Equilibrium VI.14 describes the migration of MoO_2 using $HgCl_2$ as transport agent:

$$MoO_{2,s} + HgCl_{2,g} = MoO_2Cl_{2,g} + Hg_g \qquad (VI.14)$$

The important gaseous species are Hg, MoO_2Cl_2, $MoOCl_3$, HCl, and $MoCl_4$. Only the solubilities $\Delta\lambda_i$[134] of Hg, $HgCl_2$, and MoO_2Cl_2 are large enough to cause the migration of the dioxide.

If there is metallic Mo present in the system besides MoO_2, the deposition rates of MoO_2 are diminished ($\dot{m}_{exp} = 1.1$ mg/h, 1000 → 920 °C, $c(HgCl_2) = 1.26$ mg/cm^3). Most of the transport agent reacts with the metal to form $MoCl_{2,s}$ and cannot act as the transport agent any further.[190]

Using $HgBr_2$ instead of $HgCl_2$ as transport agent[10,60] yields smaller deposition rates ($\dot{m}_{exp} = 37.6$ mg/h, 820 → 740 °C, $c(HgBr_2) = 1.55$ mg/cm^3). Experimental and calculated data are in good agreement. The migration of the dioxide can be described by taking $MoO_2Br_{2,g}$, $HgBr_{2,g}$, and Hg_g into account (see eq VI.3).

At higher temperatures another equilibrium gains significance:

$$MoO_{2,s} + H_2O_g + HgBr_{2,g} = (1/n)(MoO_3)_{n,g} + 2HBr_g + Hg_g \quad (n = 3, 4, 5) \qquad (VI.15)$$

At $\bar{T} = 620$ °C, eq VI.15 contributes 0.1% to the migration of MoO_2. Increasing $\bar{T}$ up to 1020 °C leads to a value of 5.0%.

If the migration of the dioxide is generated by HgI_2,[190] the deposition rates of MoO_2 are smaller than in the chlorine- or bromine-containing systems ($\dot{m}_{exp} = 2.2$ mg/h, 940 → 860 °C, $c(HgI_2) = 1.95$ mg/cm^3). The smaller deposition rates are caused by the equilibrium:

$$MoO_{2,s} + HgI_{2,g} = MoO_2I_{2,g} + Hg_g \qquad (VI.16)$$

The position of equilibrium favors the left side. The corresponding equilibrium with HI_g also favors the left side. Again, the gaseous species $(MoO_3)_{n,g}$ ($n = 3, 4, 5$) contribute to the migration of the dioxide:

$$MoO_{2,s} + H_2O_g + HgI_{2,g} = (1/n)(MoO_3)_{n,g} + 2HI_g + Hg_g \quad (n = 3, 4, 5) \qquad (VI.17)$$

At $\bar{T} = 940$ °C ($\Delta T = 80$ °C) the migration is distributed among MoO_2I_2 (36%), Mo_3O_9 (44%), Mo_4O_{12} (16%), Mo_5O_{15} (1%), and H_2MoO_4 (2%).

The migration of MoO_2 also occurs in the systems $Mo/MoO_2/HgX_2$ (X = Cl,[190] Br[10]) and $MoO_2/Mo_4O_{11}/HgX_2$ (X = Cl,[59] Br,[60] I[190]).

2. Mo_4O_{11}

In the past iodine[341−343] and $TeCl_4$[18,336,341−345] were used for the synthesis of Mo_4O_{11} crystals by chemical transport reactions. No systematic examinations of the transport behavior in these systems were carried out.

Using the mercury dihalides HgX_2 (X = Cl,[59] Br,[60] I[190]) one obtains Mo_4O_{11} crystals by chemical transport reactions ($T_2 \rightarrow T_1$, $T_2 > T_1$). It is not possible to obtain Mo_4O_{11} in a pure state in these transport systems. MoO_2 is always deposited along with Mo_4O_{11} in the sink.

For $HgCl_2$ as transport agent[59] we obtained rates up to 57 mg/h for the simultaneous transport of MoO_2 and Mo_4O_{11} in the first steady state ($\bar{T} = 620$ °C, $\Delta T = 80$ °C, $c(HgCl_2) = 4.30$ mg/cm^3). Depending on the starting ratio $n(MoO_2)/n(Mo_4O_{11})$ and temperature, we obtained two or three steady states of deposition. During the transport experiment, the solid in the source is oxidized until, in the final third steady state, there is only MoO_3 left:

(1) The equilibrium solids at T_2 and T_1 consist only of MoO_2 and Mo_4O_{11}. A mixture of MoO_2 and Mo_4O_{11} is deposited at the sink.

(2) The solid at T_2 consists of MoO_2 and MoO_3. At T_1 there is MoO_2 and Mo_4O_{11}. MoO_2 and Mo_4O_{11} are transported from T_2 to T_1.

(3) Equilibrium solid at T_1, MoO_2/Mo_4O_{11}, and at T_2, MoO_3. Following the deposition of MoO_3 in the sink leads to the oxidation of MoO_2 to Mo_4O_{11}.

These three cases could be investigated in more detail by using the transport balance. The mechanism of transport and deposition, depending on the mean transport temperature $\bar{T}$ and the starting ratios, is very complicated. The observed phase ratios and the sequence of deposition can be accounted for by thermochemical model calculations. It is not possible to propose a simple transport reaction for the migration of the solid phases in the system $MoO_2/Mo_4O_{11}/HgCl_2/H_2O$ (for details see ref 59).

With $HgBr_2$ as transport agent (starting solids MoO_2/Mo_4O_{11})[60] the transport system is similar. Like in the $HgCl_2$-containing transport system the solid in the source is oxidized during the transport reaction. Deposition rates up to 59 mg/h (MoO_2/Mo_4O_{11}, first steady state, 820 → 740 °C, $c(HgBr_2) = 4.30$ mg/cm^3) were observed.

In the system $MoO_2/Mo_4O_{11}/HgI_2/H_2O$ the deposition rate of the oxide is diminished to values less than 4.0 mg/h.[190] This is due to the fact that MoO_2I_2 is less stable than MoO_2Cl_2 and MoO_2Br_2. Primarily the gaseous species $(MoO_3)_{n,g}$ ($n = 3, 4, 5$) contribute to the migration of the oxides. In contrast to the $HgCl_2$- and $HgBr_2$-containing systems we observed Mo_8O_{23} and $Mo_{18}O_{52}$ besides MoO_2 and Mo_4O_{11}. Again, we recorded two steady states for some experiments.

3. MoO_3

Only a few papers have been published on the chemical transport of MoO_3 until now.

In the system MoO_3/Cl_2, the molybdenum trioxide migrates from the higher to the lower temperature according to the endothermic transport reaction:[346]

$$MoO_{3,s} + Cl_{2,g} = MoO_2Cl_{2,g} + {}^1/_2O_{2,g} \qquad (VI.18)$$

A related transport system results if Cl_2 is replaced by $HgCl_2$:[346]

$$MoO_{3,s} + HgCl_{2,g} = MoO_2Cl_{2,g} + Hg_g + {}^1/_2O_{2,g} \qquad (VI.19)$$

Glemser and Haeseler[347] reported an increased volatility of MoO_3 in a temperature range of 600–690 °C when water is present (cf., ref 348):

$$MoO_{3,s} + H_2O_g = MoO_2(OH)_{2,g} \qquad (VI.20)$$

It is also possible to obtain crystals of MoO_3 if HCl[349] or $TeCl_4$[336] are used as transport agents.

D. Oxo Compounds

1. Molybdates

General thermodynamic aspects of the chemical transport of the ternary oxides $MMoO_4$ (M = Mg, Mn, Co, Ni) with chlorine or HCl as transport agent are discussed by Emmenegger.[251]

Reichelt and Oppermann give a detailed discussion about the system Mn/Mo/O.[99] The preparation of pure $MnMoO_4$ and pure $Mn_2Mo_3O_8$ with several transport agents (Cl_2, I_2, HCl, HI, $TeCl_4$, and $SeCl_4$) are described. The composition of the equilibrium gas phases and solubilities of the solids in the gas phases were calculated using the program GMIN.

Systematic investigations of the transport system V/Mo/O with Cl_2 as transport agent[350] show that it is possible to obtain crystals of $V_9Mo_6O_{40}$ by means of chemical transport reactions, when oxygen is excluded from the system. Experiments with $TeCl_4$ as transport agent[351] are also presented.

Crystals of α-$ZnMoO_4$ can be grown using chlorine as transport agent (950 → 850 °C).[352] Moreover the crystallization of $Zn_2Mo_3O_8$ by HX (X = Cl, Br) or I_2 as transport agents (950 → 850 °C) is described.[352] Single crystals of $CuMoO_4$ and $Cu_3Mo_2O_9$ were grown with Cl_2, Br_2, HCl, and $TeCl_4$ as transport agent.[100]

Strobel *et al.* described the crystal growth of $M_2Mo_3O_8$ (M = Mn, Fe, Co, Ni) by means of $TeCl_4$.[353,354]

2. Phosphates

It is possible to obtain crystals of molybdenum(III), -(IV), and -(V) phosphates by chemical transport reactions.

$Mo(PO_3)_3$ can be crystallized by means of iodine (900 → 800 °C, $c(I_2) = 0.05$ mg/cm^3),[355] $HgBr_2$ (1000 → 900 °C, $c(HgBr_2) = 2.50$ mg/cm^3),[356] or NH_4I (1000 → 900 °C, $c(NH_4I) = 0.50$–3.00 mg/cm^3).[356] For this one can use the trimetaphosphate[355] or a mixture of MoO_3/P[356] as starting solids.

MoP_2O_7 migrates in a temperature gradient (1000 → 900 °C) by means of I_2 or $HgBr_2$.[356] Depending on the starting solids (MoO_3/P, MoO_2/P, or $Mo_2P_2O_{11}/P$) MoP or the molybdenum(V) phosphates can be deposited along with MoP_2O_7.[356]

$MoPO_5$ (800 → 650 °C, TA I_2), $Mo_4P_6O_{25}$ (800 → 650 °C, TA I_2), and $Mo_2P_4O_{15}$ (1000 → 900 °C, TA I_2; 900 → 800 °C, TA $HgCl_2$; 900 → 750 °C, TA $HgBr_2$) can be transported from hot to cold.[356] As starting solids mixtures of $Mo_2P_2O_{11}/P$ were used.

E. Intermetallic Compounds

1. Phosphides, Arsenides, and Antimonides

When $HgBr_2$ is used as a transport agent the metal-rich molybdenum phosphides Mo_3P, Mo_4P_3, and MoP as well as the pure metal can be crystallized by chemical vapor transport reactions.[357] Due to endothermic reactions the phosphides migrate in a gradient from the higher to the lower temperature.

A critical comparison of experimental observations and calculated results reveals that $MoBr_{4,g}$ and $PBr_{3,g}$ are the most important gaseous species contributing to the migration of the phosphides. Thus the migration of Mo_3P, Mo_4P_3, and MoP can be described by the following equilibria:

$$Mo_3P_s + (3n + 3)/2HgBr_{2,g} = 3MoBr_{n,g} + PBr_{3,g} + (3n + 3)/2Hg_g \quad (n = 2, 3) \quad (VI.21)$$

$$Mo_4P_{3,s} + (4n + 9)/2HgBr_{2,g} = 4MoBr_{n,g} + 3PBr_{3,g} + (4n + 9)/2Hg_g \quad (n = 2, 3) \quad (VI.22)$$

$$MoP_s + {}^7/_2HgBr_{2,g} = MoBr_{4,g} + PBr_{3,g} + {}^7/_2Hg_g \quad (VI.23)$$

Up to now this is the first metal-rich phosphide system, for which it is possible to cause a migration of all phosphides in a temperature gradient using only one transport agent. From Mo to MoP all members of this class of substances (Mo, Mo_3P, Mo_4P_3, and MoP) can be crystallized by chemical vapor transport with $HgBr_2$ as transport agent.

With MoP as the starting solid only MoP was found as the equilibrium solid in the source and the sink region. We observed deposition rates $\dot{m}$(MoP) up to 45.5 mg/h (1000 → 900 °C, $c(HgBr_2) = 7.28$ mg/cm^3). Starting with Mo_4P_3 we observed MoP besides Mo_4P_3 in the source and sink region (1050 → 950 °C). Transport rates up to 28.2 mg/h were measured ($c(HgBr_2) = 8.90$ mg/cm^3). A reduced P content of the solid (Mo_3P) lowers the transport rates ($\dot{m}(Mo_3P)$ = 9.4 mg/h, 1050 → 950 °C, $c(HgBr_2) = 5.08$ mg/cm^3). In contrast to the system MoP/$HgBr_2$ the reduction of $\bar{T}$ leads to the formation of $MoBr_2$ with Mo_4P_3 or Mo_3P as starting solids.

It is also possible to obtain crystals of Mo_4P_3 and MoP using iodine as transport agent.[356] The transport rates are considerably smaller than in the $HgBr_2$-containing system.

Single crystals of Mo_5As_4, Mo_2As_3, $MoAs_2$, and Mo_3Sb_7 were obtained by means of Cl_2,[358,359] Br_2,[358,359] or I_2.[358−361] Murray *et al.*[359] investigated the transport systems Mo/As/X (X = Cl, Br, I) systematically and obtained the following transport equilibria (X = Br):

$$MoAs_{2,s} + 2Br_{2,g} = MoBr_{4,g} + {}^1/_2As_{4,g} \quad (VI.24)$$

$$Mo_2As_{3,s} + 4Br_{2,g} = 2MoBr_{4,g} + {}^3/_4As_{4,g} \quad (VI.25)$$

2. Chalcogenides

a. Sulfides. Like many other transition metal sulfides MoS_2 can be transported with sulfur as transport agent (800 → 700 °C).[272,362] Moreover, crystals of Mo_2S_3 and MoS_2 could be also obtained with halogens (Cl_2,[1] Br_2,[362−364] and I_2[317]) or halides (HBr,[363] NH_4Br,[363] MBr_2 (M = Ge, Sn)[363]) as transport agents. Except for iodine, details of the transport processes have not been examined. MoS_2 transports via MoO_2I_2, when iodine is added as transport agent and moisture is present in the system ($\dot{m}(MoS_2)$ = 0.5 mg/h, 820 → 750 °C, $c(I_2) = 3.81$ mg/cm^3).[317]

$$MoS_{2,s} + 2H_2O_g + 3I_{2,g} = MoO_2I_{2,g} + 4HI_g + S_{2,g} \quad (VI.26)$$

$PbMo_6S_8$ can be transported with $PbCl_2$ as transport agent (e.g., 1100 → 1000 °C).[365]

b. Selenides and Tellurides. The semiconducting $MoSe_2$ has been subjected to many investigations since it proved to be interesting for solar energy conversion. Therefore the influence of some transport agents on the growth of large single crystals of $MoSe_2$ was investigated (Se,[362,366−368] Br_2,[1,362,364,367,368,371] I_2,[1,367,368] $SeCl_4$,[367,368] and $TeCl_4$[367,368]).

Legma *et al.*[367] established that $MoSe_2$ migrates via $MoSe_3$, when selenium is added as transport agent (1020 → 980 °C, c(Se) = 9.00 mg/cm^3). No transport rates are published in this paper.

$$MoSe_{2,s} + Se_g = MoSe_{3,g} \quad (VI.27)$$

According to the same authors[367] the migration of $MoSe_2$ with Br_2 (910 → 870 °C, $c(Br_2) = 1.00$ mg/cm^3) and I_2 (930 → 830 °C, $c(Br_2) = 3.00$ mg/cm^3) as transport agents should be determined by the following equilibrium:

$$MoSe_{2,s} + {}^3/_2X_{2,g} = MoX_{3,g} + Se_{2,g} \quad (X = Br, I) \quad (VI.28)$$

However, from our point of view it seems more likely, that the metal migrates via $MoBr_4$ with bromine as transport agent and via MoO_2I_2 (H_2O from the silica ampule) with iodine, respectively. For the migration of $MoSe_2$ in the presence of $SeCl_4$ (1020 → 980 °C) and $TeCl_4$ (1000 → 850 °C) no transport equilibria were reported.

Crystals of the mixed-transition metal dichalcogenides $Mo_{1-x}W_xSe_2$ and $Mo_{1-x}W_xTe_2$ can be obtained in an endothermic transport process, when bromine is added.[369,370]

$MoTe_2$ migrates from hot to cold by means of Br_2 (900 → 700 °C),[1,362,370−373] I_2 (770 → 750 °C),[374] or $TeCl_4$.[375]

VII. Tungsten

A. Metal

Due to the significance of tungsten in transport reactions in halogen lightbulbs, many papers have been published concerning this field (see for example refs 376−378). For that reason the list of literature in Table 3 cannot be considered as complete. Most of these investigations were carried out at temperatures ranging from 3000 to 300 °C.

As for molybdenum most of the transport reactions in the similar tungsten-containing system are exothermic causing the metal to migrate from the zone of the lower to the one of the higher temperature ($T_1 \rightarrow T_2$, $T_2 > T_1$).

The transport of tungsten in iodine-containing systems[317,379] is an example of a W-containing exothermic transport system and should be particularly mentioned. Tungsten can only be transported by means of iodine if water is present besides the halogen. Equilibrium VII.1 describes the migration of the metal.

$$W_s + 2H_2O_g + 6I_g\ (3I_{2,g}) = WO_2I_{2,g} + 4HI_g \quad (VII.1)$$

To the best of our knowledge there are only a few examples of systems (W/$HgBr_2$[11] and W/HgI_2[190]) transporting the metal into the low-temperature region of the ampule.

With $HgBr_2$ as transport agent we obtained deposition rates of tungsten up to 41 mg/h (1000 → 900 °C, $c(HgBr_2) = 4.25$ mg/cm^3). In contrast to molybdenum the tungsten metal migrates as single phase. Neither WO_2 nor WBr_2 was formed by reaction of W with H_2O or $HgBr_2$ at T_2 or T_1. WO_2Br_2 has the largest partial pressure of all tungsten-containing gaseous species, but because of its small $\Delta\lambda_i$ value[134] it does not contribute to the migration of tungsten.

The equilibria VII.2 and VII.3 cause the endothermic migration of W:

$$W_s + 2HgBr_{2,g} = WBr_{4,g} + 2Hg_g \quad \text{(VII.2)}$$

$$W_s + {}^5/_2HgBr_{2,g} = WBr_{5,g} + {}^5/_2Hg_g \quad \text{(VII.3)}$$

At $\bar{T} = 800$ °C ($\Delta T = 100$ °C) WBr_4 contributes 4.3% and WBr_5 93.5% to the migration of the metal. At higher temperatures (1100 → 1000 °C) the amount of WBr_5 is reduced (WBr_4 59.5%, WBr_5 37.5%).

Introducing oxygen in the form of H_2O or WO_2 into the system increases the WO_2Br_2 pressure while the $HgBr_2$ pressure and the transport rates ($\dot{m}(W) < 1.0$ mg/h) become smaller. This time the deposition of WO_2 in a first steady state is followed by the migration of W in a second step.

With W or W/WO_2 (TA $HgBr_2$) as starting solids we observed a delayed deposition of tungsten (i.e., $\bar{T} = 800$ °C, 15 h delay of deposition) (Figure 4).

By means of HgI_2 tungsten also migrates from T_2 to T_1. In contrast to the system W/$HgBr_2$ the deposition rates are very small ($\dot{m}_{exp} = 0.2$ mg/h, 920 → 840 °C, $c(HgI_2) = 1.68$ mg/cm^3). In addition to the metal, a small amount of tungsten dioxide is deposited in the sink in a first steady state. The endothermic equilibrium VII.4 regulates the migration of W. The dioxide is formed by the metal reacting with water out of the wall of the ampule (or impurities of the chemicals).

$$W_s + 2H_2O_g + 3HgI_{2,g} = WO_2I_{2,g} + 4HI_g + 3Hg_g \quad \text{(VII.4)}$$

B. Halides and Oxyhalides

During the research on the transport reactions in halogen bulbs the tungsten halide and oxyhalide systems were also investigated. In order to obtain the thermodynamic data of these compounds it was necessary to synthesize pure samples. Again, chemical transport reactions are a good means of purifying the starting materials.

WBr_2 can be transported, when WBr_4[380] or $HgBr_2$[11] are added. The migration caused by chemical transport reactions is accompanied by sublimation.

$WOBr_2$ and $WOBr_3$ can be prepared by reaction of tungsten metal with WO_3 and bromine. The tungsten oxybromides can be purified in the following transport reaction, which may be accompanied by sublimation ($WOBr_2$, 580 → 450 °C; $WOBr_3$, 400 → 350 °C), with excess bromine as transport agent:[381−383]

$$WOBr_{2,s} + WOBr_{4,g} = 2WOBr_{3,g} \quad \text{(VII.5)}$$

$$WOBr_{3,s} + WBr_{6,g} = WOBr_{4,g} + WBr_{5,g} \quad \text{(VII.6)}$$

Crystals of $Se_{17}(WCl_6)_2$,[384] $Te_4(WCl_6)_2$,[385,386] $Te_6(WOCl_4)_2$,[387] Te_7WOCl_5,[388] Te_7WOBr_5, [389] $Te_8[WCl_6]_2$,[390] $[Te_{15}X_4][WOX_4]_2$ (X = Cl, Br),[328] $(Se_6I)WCl_6$,[391] and $Te_6I_2(WCl_6)_2$[390] can be crystallized by transport reactions ($T_2 = 250-150$ °C, $T_1 = 210-125$ °C, $\Delta T = 20-70$ °C) which may be accompanied by sublimation as well.

C. Oxides

1. Dioxide

By using the halogens (Cl_2,[392,393] Br_2,[190] I_2[317,329,332,379,394−396]) as transport agents tungsten dioxide migrates to the zone of lower temperature of the ampule. The transport of WO_2 proceeds via WO_2X_2 (X = Br, I) and can be described by the equilibrium

$$WO_{2,s} + X_{2,g} = WO_2X_{2,g} \qquad (X = Br, I) \qquad \text{(VII.7)}$$

Kleber *et al.*[393] reported an endothermic transport using $X_2 = Cl_2$ ($T_2 = 1000-850$ °C, $T_1 = 950-750$ °C). Our model calculations[190] demonstrate that a transport from the hotter into the cooler region of an ampule is only possible if water is present in the system. In this case HCl instead of Cl_2 causes the endothermic transport of WO_2.

$$WO_{2,s} + 2HCl_g = WO_2Cl_{2,g} + H_{2,g} \quad \text{(VII.8)}$$

Furthermore our model calculations confirm the exothermic reaction of WO_2 in the absence of water. Maintaining these experimental conditions is difficult as the wall of the silica ampule releases water at high temperatures.[2]

Bromine as transport agent[190] leads to the deposition of $W_{18}O_{49}$ besides WO_2 at T_1; the deposition rates are quite small ($\dot{m}_{exp}(WO_2 + W_{18}O_{49}) = 1.7$ mg/h, 840 → 760 °C, $c(Br_2) = 0.39$ mg/cm^3).

Experimental results of the transport system WO_2/I_2 are presented in several papers.[317,329,332,379,394−396] Dettingmeijer *et al.* reported transport rates up to 14 mg/h.[379] Experimental results as reported by Schäfer *et al.* were $\dot{m}_{exp}(max) = 86$ mg/h ($c(I_2) = 3.05$ mg/cm^3, 1000 → 800 °C).[317] Moreover, a small amount of $W_{18}O_{49}$ ($WO_{2.72}$) is also deposited at T_1.

Using $HgCl_2$[62] as transport agent we observed transport rates up to 4.5 mg/h ($c(HgCl_2) = 14.17$ mg/cm^3, 950 → 850 °C). In addition to WO_2, $W_{18}O_{49}$ is formed as an additional equilibrium solid at T_1. The amounts of $W_{18}O_{49}$ however are small. According to our model calculations the transport of WO_2 is described by equilibrium VII.9 at low temperatures ($\bar{T} = 590$ °C).

$$WO_{2,s} + HgX_{2,g} = WO_2X_{2,g} + Hg_g \quad (X = Cl, Br, I) \quad \text{(VII.9)}$$

At higher temperatures ($\bar{T} = 950$ °C) HCl, formed by reaction of $HgCl_2$ with H_2O, takes on greater

Table 3. Chemical Transport of Tungsten and Tungsten Compounds[a]

substance	transport agent	ref(s)
W	Cl_2 (−)	315,378,429–432
	Br_2 (−)	433,434
	I_2; I_2/H_2O (+)	317,379
	H_2O (+)	317,435–440
	O/O_2 (−/+)	441
	X_2 (X = F, Cl, Br, I) (−)	442
	X_2 (X = F, Cl, Br) (−)	443,444
	X/O (X = F, Cl, Br, I) (−)	377,445,446
	HX (−)	447,448
	X/H/O (X = F, Cl, Br) (−)	449–453
	F/O (−)	454,455
	F containing systems (−)	456–458
	$HgBr_2$ (+)	11
	HgI_2 (+)	190
	WCl_6/Cl_2 (−)	459
	PSX_3 (X = Cl, Br) (−)	460,461
	CH_2Br_2 (−)	462
Mo/W	$HgBr_2$ (+)	155
WP	I_2 (+)	417,418
WP_2	I_2 (+)	417
W_2As_3	I_2 (+)	360
WAs_2	I_2 (+)	360
WO_2	Cl_2 (+)	392,393
	Br_2 (+)	190
	I_2 (+)	317,329,332,379,394–396
	HCl (+)	392,393
	$TeCl_4$ (+)	335,397
	$TeBr_4$ (+)	335
	$HgCl_2$ (+)	62
	$HgBr_2$ (+)	11,14,62
	HgI_2 (+)	63
	H_2O/H_2 (+)	1,398,399
	NH_4Cl (+)	190
$W_{18}O_{49}$	I_2/H_2O (+)	379
	$TeCl_4$ (+)	397
	HgX_2 (X = Cl, Br) (+)	62
	HgI_2 (+)	63
$W_{20}O_{58}$	Cl_2 (+)	393
	HCl (+)	393
	$TeCl_4$ (+)	397
WO_3	Cl_2 (+)	400–402
	Br_2 (+)	401,402
	H_2O (+)	347,398,400,403–405
	HCl (+)	400–402,407
	CCl_4 (+)	400
	$TeCl_4$ (+)	397
	$HgCl_2$ (+)	64
$ZnWO_4$	Cl_2 (+)	251,282
	HCl (+)	251
MWO_4 (M = Mg, Mn, Fe, Co, Ni)	Cl_2 (+)	251
	HCl (+)	251
In_2WO_4	H_2O (+)	412
A_xWO_3 (A= K, Rb, Cs; HTB, TTB, ITB)	HgX_2 (X = Cl, Br) (+)	413–415
$A_xNb_yW_{1-y}O_3$ (A= K, Rb; ITB)	HgX_2 (X = Cl, Br) (+)	414
$Ge_{0.24}WO_3$ (HTB)	H_2O (+)	416
$V_{1-x}W_xO_2$	$TeCl_4$ (+)	408
$(V,W)O_x$	HCl (+)	409,410
$(Nb,W)O_x$	$HgCl_2$ (+)	411
WP_2O_7	I_2 (+)	417
WPO_5	I_2 (+)	417
WS_2	S_2 (+)	272
	Cl_2 (+)	419
	Br_2 (+)	364,419
	I_2 (+)	317
WSe_2	Se (+)	362,367,368,420
	Br_2 (+)	1,362,364,367,368,371,372,420–422
	I_2 (+)	1,367,368,371,421,424–426
	$SeCl_4$ (+)	367,368,428
	$TeCl_4$ (+)	367,368
WSSe	I_2 (+)	427
WTe_2	Br_2 (+)	1,362,371,372
	I_2 (+)	1,371
WBr_2	Br_2 (+)	380
	$HgBr_2$ (+)	11
$WOBr_3$	Br_2 (+)	381,383
$WOBr_2$	Br_2 (+)	382,383

Table 3 (Continued)

substance	transport agent	ref(s)
$Se_{17}(WCl_6)_2$	autotransport (+)	384
$Te_4(WCl_6)_2$	autotransport (+)	385
$Te_6(WOCl_4)_2$	autotransport (+)	386
$Te_6I_2(WCl_6)_2$	autotransport (+)	386
Te_7WOCl_5	autotransport (+)	388
Te_7WOBr_5	autotransport (+)	389
$Te_8[WCl_6]_2$	autotransport (+)	390
$(Se_6I)WCl_6$	autotransport (+)	391
$[Te_{15}X_4]_n[WOX_4]_{2n}$ (X = Cl, Br)	autotransport (+)	328

[a] Key: (+) $T_2 \rightarrow T_1$ "endothermic transport", (−) $T_1 \rightarrow T_2$ "exothermic transport" ($T_2 > T_1$).

influence as a transport agent compared to $HgCl_2$. The released $O_{2,g}$ is fixed in the solid in form of $W_{18}O_{49}$. Now the transport of WO_2 is determined by eq VII.8. The transport mechanism is discussed by Schornstein and Gruehn.[62]

The similar transport system containing $HgBr_2$ is much more efficient than the one containing $HgCl_2$ $\dot{m}_{exp}(max) = 1195$ mg/h, 840 → 760 °C, $c(HgBr_2) = 9.19$ mg/cm^3).[11,14,62] Experimental results can be accounted for by thermochemical calculations, thus the transport of WO_2 can be described by eq VII.9.[14] As for W, we observed a delay of deposition of WO_2 at low mean transport temperatures (cf., Figure 4). At lower temperatures the experimental transport rates become smaller than those based on the model calculations (cf., Figure 2). It could be demonstrated that the deposition of WO_2 at T_1 is kinetically hindered.[14]

With HgI_2 instead of $HgBr_2$ deposition rates up to 72.4 mg/h (960 → 880 °C, $c(HgI_2) = 8.54$ mg/cm^3) were measured.[63] The use of a mixture of W and WO_2 as starting solids at T_2 leads to the deposition of pure WO_2 in the sink region. $W_{18}O_{49}$ is formed at T_2 and migrates to the zone of lower temperature, if no W is added. The transport of WO_2 is described by reaction VII.9.

Tungsten dioxide migrates by means of HCl (see eq VII.8) in an endothermic transport reaction.[392,393] Therefore it is possible to transport WO_2 using NH_4Cl as transport agent.[190] While migrating, the dioxide is partially reduced, forming metallic tungsten, which is observed at T_2 as an equilibrium solid and is the only solid to migrate into the sink region ($\dot{m}_{exp}(max) = 21.5$ mg/h, 1025 → 925 °C, $c(NH_4Cl) = 0.47$ mg/cm^3).

Tellurium tetrahalides TeX_4 (X = Cl,[335,397] Br[335]) have a considerable effect on the transport of WO_2 ($\dot{m}_{max} = 22.0$ mg/h, TA $TeCl_4$, $\dot{m}_{max} = 40.0$ mg/h, TA $TeBr_4$). A comparison of the experimentally observed and the calculated transport rates is given.[335,397]

Several authors[1,398,399] report on the evaporation of WO_2 at high temperatures in the presence of a mixture containing H_2O/H_2.

2. $W_{18}O_{49}$ and $W_{20}O_{58}$

$W_{18}O_{49}$ and $W_{20}O_{58}$ can be crystallized in a temperature gradient ($T_2 \rightarrow T_1$, $T_2 > T_1$) by employing several transport agents [Cl_2,[393] HCl,[393] I_2/H_2O,[379] $TeCl_4$,[397] and HgX_2 (X = Cl, Br, I)[63]].

Transport experiments with $WO_2/W_{18}O_{49}$ as starting phases reveal that $HgBr_2$ and $HgCl_2$ are suitable transport agents.[62] Experimental and calculated results agree to a large extent, if the presence of small amounts of H_2O and the resulting gaseous species (for example HCl or HBr), formed under equilibrium conditions, as well as an influence of convection, are taken into consideration.

The migration of $W_{18}O_{49}$ in the transport system $WO_2/W_{18}O_{49}/H_2O/HgI_2$ was compared with detailed model calculations.[63] Starting with $WO_2/W_{18}O_{49}$, tungsten dioxide is transported prior to $W_{18}O_{49}$ in a first steady state. For $W_{18}O_{49}$ transport rates up to $\dot{m} = 47.0$ mg/h were measured. Thermodynamic calculations reveal that the transport of $W_{18}O_{49}$ is expressed by several endothermic equilibria involving small amounts of H_2O from the silica ampule.

$$WO_{2.72,s} + HgI_{2,g} + 1.44HI_g = WO_2I_{2,g} + Hg_g + 0.72H_2O_g + 0.72I_{2,g} \quad \text{(VII.10)}$$

$$WO_{2.72,s} + HgI_{2,g} + 0.72H_{2,g} = WO_2I_{2,g} + Hg_g + 0.72H_2O_g \quad \text{(VII.11)}$$

$$WO_{2.72,s} + 2HI_g = WO_2I_{2,g} + 0.28H_{2,g} + 0.72H_2O_g \quad \text{(VII.12)}$$

For the transport of $W_{20}O_{58}$ with HCl or $TeCl_4$ only the experimental data are published.[397]

3. Tungsten Trioxide

By means of chemical transport reactions it is possible to obtain crystals of WO_3. In the past transport reactions were used only to crystallize WO_3 as single phase. Only a few papers are concerned with thermochemical calculations on the transport.

By means of chlorine[400−402] or bromine[401,402] tungsten trioxide migrates according to eq VII.13:

$$WO_{3,s} + X_{2,g} = WO_2X_{2,g} + {}^1\!/_2O_{2,g} \qquad (X = Cl, Br) \quad \text{(VII.13)}$$

Like MoO_3, the volatility of WO_3 is increased in the presence of water[347,398,400,403−406] (see eq VII.14):

$$WO_{3,s} + H_2O_g = WO_2(OH)_{2,g} \quad \text{(VII.14)}$$

With CCl_4,[400] HCl,[400−402,407] or $TeCl_4$[397] as transport agents there is a transport effect, too. At high temperatures, the decomposition of CCl_4 leads to the formation of Cl_2.

Schornstein and Gruehn[64] investigated the transport system $WO_3/HgCl_2$ comparing the experimental results with those based on thermochemical calculations. WO_3 migrates by means of $HgCl_2$ with transport rates up to 64.8 mg/h (1140 → 1060 °C, $c(HgCl_2)$ = 1.11 mg/cm^3).

$$WO_{3,s} + HgCl_{2,g} = WO_2Cl_{2,g} + Hg_g + {}^1/_2O_{2,g} \quad (VII.15)$$

Furthermore the effects of the transport agents HgX_2, X_2 (X = Cl, Br, I), and HCl on the deposition rate of WO_3 are compared.[64] It is concluded from these data that chlorine has the largest transport effect at temperatures up to ~920 °C, whereas $HgCl_2$ is more effective at higher temperatures.

It is possible to obtain mixed crystals of the composition $V_{1-x}W_xO_2$ (TA $TeCl_4$[408]). Crystals of vanadium tungsten oxides $(V,W)O_x$ (850−750 → 800−700 °C, TA Cl_2[409,410]) as well as tungsten-rich solid solutions of $(Nb,W)O_x$ phases (1250−1270 → 1100−1200 °C, TA Cl_2[411]), both having block structures, can be transported.

D. Oxo Compounds

1. Tungstates

Crystals of MWO_4 (M = Zn,[251,282] Mg,[251] Mn,[251] Fe,[251] Co,[251] Ni[251]) grow in a temperature gradient ($T_2 \rightarrow T_1$), when Cl_2 or HCl are added as transport agents. A general discussion of chemical transport of tungstates is presented by Emmenegger.[251]

In_2WO_4 migrates from hot to cold (starting solids $In_2O_3/WO_3/W$, 1100 → 1050 °C) with H_2O as transport agent.[412]

It is also possible to obtain crystals of hexagonal, tetragonal, or intergrowth tungsten bronzes (HTB, TTB, or ITB) A_xWO_3, $A_xNb_yW_{1-y}O_3$ (A = K, Rb, Cs, 800 → 750−700 °C, TA $HgCl_2$ or $HgBr_2$[413−415]) or $Ge_{0.24}WO_3$ (930 → 830 °C, TA H_2O[416]).

2. Phosphates

WPO_5 and WP_2O_7 migrate in a temperature gradient with iodine as transport agent, if WP is present.[417] Details are discussed in the next section.

E. Intermetallic Compounds

1. Phosphides and Arsenides

Of the known tungsten phosphides, only WP[417,418] and WP_2[417] can be crystallized by means of the chemical transport method using iodine as transport agent.

The reduction of WO_3 by elemental phosphorus at 800 °C leads to the formation of WP, WP_2, WPO_5, and WP_2O_7, depending on the molar ratio $n°(P)/n°(WO_3)$.[417] By chemical transport reactions using iodine as transport agent (e.g., 1000 → 900 °C, $c(I_2)$ = 5−17 mg/cm^3), the phosphides and phosphates can be purified and crystallized.

$$WP_s + 2H_2O_g + I_{2,g} = WO_2I_{2,g} + {}^1/_4P_{4,g} + 2H_{2,g} \quad (VII.16)$$

$$WP_{2,s} + 2H_2O_g + I_{2,g} = WO_2I_{2,g} + {}^1/_2P_{4,g} + 2H_{2,g} \quad (VII.17)$$

The observed simultaneous transport of WP and WPO_5 implies that the following equilibrium may play a major part in the chemical transport reactions with tungsten phosphates.

$$^{14}/_5WPO_{5,s} + {}^6/_5WP_s + 4I_{2,g} = 4WO_2I_{2,g} + P_4O_{6,g} \quad (VII.18)$$

After Martin and Gruehn[418] WP as well as many other phosphides can be prepared by reduction of WO_3 with aluminum in the presence of phosphorus in sealed silica ampules ($T \approx$ 500 °C).

Crystals of WP can be separated from the reaction mixture by subsequent chemical transport ($\dot{m}(WP)$ = 1.1 mg/h, 1000 → 900 °C, $c(I_2)$ 14.2 mg/cm^3) in the synthesis ampule.

Single crystals of W_2As_3 and WAs_2 were obtained with Br_2[358] or I_2[360] as transport agents.

2. Chalcogenides

a. Sulfides. WS_2 migrates from hot to cold (800 → 700 °C) similar to MoS_2, when excess sulfur is present in the system.[272] It is not quite clear by which gaseous species this transport is mediated. Crystals of WS_2 can be grown by means of Cl_2,[419] Br_2,[364,419] or I_2.[317]

Schäfer *et al.*[317] investigated the transport system $WS_2/I_2/H_2O$ obtaining transport rates up to $\dot{m}(WS_2)$ = 16.7 mg/h (900 → 700 °C, $c(I_2)$ = 1.18 mg/cm^3). It is concluded in this paper that the migration of WS_2 proceeds via WO_2I_2 and S_2, while I_2, in combination with H_2O, reacts as transport agent.

$$WS_{2,s} + 2H_2O_g + 3I_{2,g} = WO_2I_{2,g} + 4HI_g + S_{2,g} \quad (VII.19)$$

b. Selenides and Tellurides. The semiconducting WSe_2, WSSe, and WTe_2 have been the subjects of many investigations as have the analogous molybdenum compounds. For the crystallization of the selenides and the telluride, many transport agents were used (Se,[362,367,368,420] Br_2,[1,362,364,367,368,370−372,420−423] I_2,[1,367,368,371,421,424−427] $SeCl_4$,[367,368,428] and $TeCl_4$[367,368,423]).

With selenium as transport agent (e.g., 1000 → 850 °C, $c(Se)$ = 9.00 mg/cm^3) the transport of WSe_2 may be caused by $WSe_{3,g}$[367] (eq VII.20). No transport rates are reported.

$$WSe_{2,s} + Se_g = WSe_{3,g} \quad (VII.20)$$

With Br_2 (910 → 870 °C, $c(Br_2)$ = 1.00 mg/cm^3) and I_2 (800 → 750 °C, $c(I_2)$ = 1.00 mg/cm^3) the transport is described by the following endothermic equilibrium:[367]

$$WSe_{2,s} + {}^3/_2X_{2,g} = WX_{3,g} + Se_{2,g} \qquad (X = Br, I) \quad (VII.21)$$

This equilibrium, as well as the similar molybdenum-containing system, does not describe the transport behavior well. It is rather more likely that the transport of WSe_2 proceeds via WBr_4 and WBr_5 with Br_2 as transport agent and WO_2I_2 in the iodine system, respectively.

For $SeCl_4$ (1020 → 980 °C, $c(SeCl_4)$ = 3.00 mg/cm^3) and $TeCl_4$ (1000 → 850 °C, $c(TeCl_4)$ = 3.00 mg/cm^3) only the experimental data are given.

Crystals of $Mo_{1-x}W_xSe$[369] and $WSSe$[427] can be obtained with bromine and iodine as transport agents.[367]

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