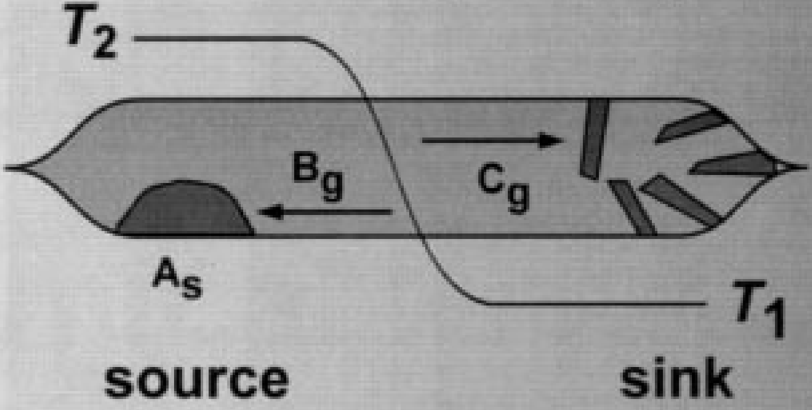
Chemical Transport Reactions

$$A_s + B_g = C_g$$



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Chlorides Fluorides

Silicides Phosphates

Sulfates (Ln, U, Th) / M / O

Ln / M / O / Cl

Niobates Oxides

Phosphides

Intermetallics

New Results of Chemical Transport as a Method for the Preparation and Thermochemical Investigation of Solids

Reginald Gruehn* and Robert Glaum

Dedicated to Professor Arndt Simon on the occasion of his 60th birthday

Chemical transport experiments are a valuable aid of great potential in the synthesis and thermochemical characterization of solids. Compounds of interest can often only be crystallized by this method. The use of a transport balance allows very detailed observations, particularly of the course of the experiment over time (simultaneous or sequential deposition of multiple-phase solids). The computer program CVTRANS enables a quantitative thermochemical description of the experiment based on the cooperative transport model. A compilation of recent results illustrates the development and efficiency of the method. The transport of phosphides, anhydrous phosphates and sulfates, and rare-earth oxide and oxohalide compounds are treated in detail.

Keywords: chemical transport · crystal growth · lanthanides · thermochemistry · transition metals

1. Introduction

Transport phenomena can have various causes. The most familiar is the *physical* transport of energy in various forms; as heat, electricity, or as electromagnetic radiation. Material transport as a physical process is of fundamental significance to chemistry. Important well-known examples include separation and mixing processes, ion migration in electrolytes, or the diffusion of components of an alloy. Physical transport can also be observed in a fridge: humidity migrates by sublimation or distillation of the water to the cooler parts of the unit to form ice. The same process is also utilized for freeze-drying.

In contrast we speak of *chemical* transport when a solid (or liquid) phase (A), that is not normally volatile under the given (temperature) conditions, migrates over a temperature gradient, or more precisely over a thermochemical potential gradient, as a result of a reversible reaction [Eq. (1)] with an added gaseous substance (B) to form a gaseous product (C).

$$A_{s,l} + B_g \rightleftharpoons C_g \qquad (1)$$

In this way phase A, which is introduced at a defined position in the system, becomes mobile as part of the gaseous compound C and can be deposited at another position, that is at another temperature or at a lower thermochemical potential, by means of the back reaction according to Equation (1). The resulting "transport" of A to another location can proceed to completeness in a closed system given sufficient time, since the "transport agent" B is not consumed. A low concentration of the transport agent (TA) is usually sufficient. Chemical transport (CT) is therefore not always easy to recognize as such.

The significance of natural, *mineral-forming transport processes*, in which a usually very slow deposition from the gas phase leads to formation of large single crystals of a mineral [e.g. A in Eq. (1)] was recognized for the first time in the middle of the 19th century. In 1846 Bunsen described how Fe_2O_3 can be transported in flowing HCl after studying volcanoes on Iceland.[1] Please refer to Table 1 for other important experiments originating from this period.

A classical example of chemical transport from a modern viewpoint is the *industrial purification of Ni* developed in 1890 by Mond and Langer, in which the metal is vaporized as nickel tetracarbonyl and then deposited again at slightly higher temperatures.[5]

Research into chemical transport processes received a new impulse in 1925 by van Arkel and De Boer.[6, 7] The very intensive developments that continue to the present day began in 1950 with the work of Harald Schäfer and his coworkers. They defined for the first time, reactions as in Equation (1) as "chemical transport reactions" (CTR). Qualitative and quantitative methods of analysis were developed that were easy to understand and easy to use. Further questions on chemical transport were taken up and advanced by scientists from the group of H. Schäfer (H. Wiedemeier, M. Binnewies, R. Gruehn, and his student R. Glaum, see Table 1).

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Table 1. Developments in chemical transport.

Year	Development	Authors
1850–1890	migration of Fe_2O_3 in a HCl flow	Bunsen[1]
	"artificial formation of minerals"	Saint-Claire Deville[2]
	transport of Si and Al via the subchlorides with the addition of gaseous $SiCl_4$ or $AlCl_3$	Troost, Hautefeuille[3, 4]
	industrial purification of Ni by vaporization as $Ni(CO)_4$ and decomposition at a slightly higher temperature	Mond, Langer[5]
1925–1930	vaporization of metals with iodine and decomposition of the iodides over a glowing wire	van Arkel, De Boer[6, 7]
	transport of Au with Cl_2	Biltz, Fischer, Juza[8]
from 1950	wide-ranging investigation into fundamentals and many systems, review (up to 1962)[9] publication list up to 1987[10]	H. Schäfer
from 1960	chalcogenides	R. Nitsche[11, 12]
from 1965	thermochemistry of transport; quantitative treatment of the deposition of compounds with a homogeneity range, crystal growth (also under zero gravity)	H. Oppermann, G. Krabbes[13]
from 1970	fundamentals and examples	Faktor, Garrett[14]
from 1970	chalcogenides, crystal growth (also under zero gravity)	H. Wiedemeier[15, 16]
from 1993	CT of intermetallic phases	M. Binnewies[17]
from 1975	"transport balance",[18] "cooperative transport model",[19] Transport of anhydrous sulfates[20]	R. Gruehn
from 1986	thermodynamic treatment of transport reactions; CT of phosphides and phosphates	R. Glaum[21–23]

In addition, a large number of scientists, who cannot all be named here, have contributed to the development of the method since the beginning of the 1960s by using CT for specific investigations and, in particular, to obtain single crystals for X-ray structure analysis. At this point, it should be noted that A. Simon, who was also a student of H. Schäfer, was able to obtain analytically perfect[24] $NbCl_{2.33}$ crystals for the first time by means of chemical transport reactions in 1964 and by doing so was able to show conclusively that the composition of $NbCl_2$ was not correct.[25]

2. Chemical Transport on a Laboratory Scale

2.1. Experiments in Closed Systems with Temperature Gradients

Regarding CT as an experimental laboratory method leads to restrictions of the subject. Reversible reactions between gaseous and solid substances as in Equation (1) can take place in *open or closed systems*. Natural processes, such as the aforementioned crystallization of Fe_2O_3, typically occur in "open systems". In an industrial plant, which precludes the use of an open system, the reaction gas will be recirculated wherever possible, as with the transport agent CO in the well-known Mond process. Similar laboratory experiments can be considered as so-called "carrier gas experiments", in which data on the vaporization equilibria can be measured with the help of a flowing gas; in this case a gas circulation loop is not necessary. The possibility to deposit solids as layers of given composition, based on reversible volatility equilibria is extremely important for technical applications. If a solid A is to be deposited by the decomposition of C_g into A_s and B_g in such a process [the reverse reaction according to Eq. (1)], it will often be unnecessary to prepare the required gas component C by a reaction of A_s with B_g [forward reaction Eq. (1)]. Instead, C is introduced directly into the gas flow

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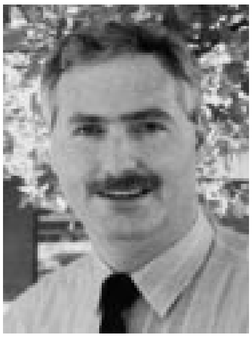
R. Gruehn



R. Glaum

Robert Glaum, born in 1960, grew up in Altenstadt/Hessen, studied chemistry at the Justus-Liebig-Universität in Giessen and at the Westfälische Wilhelms-Universität Münster, he completed his doctorate in 1990 with R. Gruehn in Giessen. After a one-year (1993/94) research visit with a Feodor-Lynen stipendium from the Alexander-von-Humboldt Foundation to M. Hitchman (University of Tasmania, Australia), he completed his habilitation in inorganic chemistry in 1999 at the Department of Chemistry of the Justus-Liebig-Universität Giessen. His research interests include the synthesis, structural chemistry, and physical characterization (color, magnetism) of anhydrous transition metal phosphates and the preparative and methodological development of the chemical transport method.

and A_s will be formed at the required position by appropriate adjustment of the pressure and temperature. This procedure, which is referred to as chemical vapor deposition (CVD), is used in many variations for technical purposes. We will not regard this subject further in this review.

In the laboratory, closed systems with *temperature gradients* have proven to be particularly valuable. In our research group, following a procedure already described by Schäfer,[26] chemical transport experiments in silica glass ampoules ($l \approx$ 12 cm, $d \approx 1.5$ cm, wall thickness ca. 1.5 mm) are carried out in electrically heated and electronically regulated two-zone tubular furnaces ($T_{max} = 1150\,^{\circ}C$). The pressure in the silica glass ampoules should not exceed 10 atm for the given dimensions. The use of other ampoule materials for transport experiments at temperatures far above 1000 °C has been described by Kaldis.[27, 28]

2.2. Objectives and Possibilities of Transport Experiments

A substance that is to be transported is "dissolved" at the temperature of the "source" where it was introduced, according to Equation (1), and because of the reversibility of the reaction at the temperature of the "sink", deposited once more, usually in a well-crystallized form. *Preparative experiments* can be performed in this way under clear, "defined" conditions, and lead to easily reproducible results, amongst other advantages. When the thermodynamic data of all participating components are known, predictions can be made about the kind of phases produced and about the order of magnitude of the rates of deposition. Often certain predictions and estimations can still be made even if not all the thermodynamic data are available. Also, the results of transport experiments allow the *delimitation of thermodynamic data* of the participating solids or gas molecules.

It is often possible to obtain solids in the sink as pure phases, whereas complete reaction is difficult in conventional solid-state reactions, or necessarily only at much higher temperatures. Transport methods are favorable in comparison to crystallization from solutions or melts because usually only very little "transport agent" is required, which is in most cases gaseous, so that impurities in the crystals can be easily prevented.

2.3. Experiments under Isothermal Conditions

In certain cases, experiments without an externally applied temperature gradient can also be useful.[29] In such a case, the substance to be crystallized (A_s) is heated together with the transport agent (B_g) in a very short ampoule ($l \sim 3$ cm). If the equilibrium conditions [Eq. (1)] are favorable, a type of "*short-path transport*" between the crystallites or the particles of a powder (A), for example, in connection with a (thermodynamically favorable) particle or crystal growth occurs. The role of an applied gaseous "mineralizer" in small quantities can also be used with advantage to establish equilibrium between the components of a multiple-substance system (several solid phases), particularly when binary or multicomponent phases are to be formed during the experiment from the solid starting materials. In this manner, phase equilibria, for example in a three-phase system, can be investigated under temperature conditions under which no reaction between the reactants would be expected without the presence of the mineralizer. Examples from our research include the *elucidation of the phase relationships* between Ln_2O_3, $LnCl_3$ and various metal oxides (see Section 8) and the investigation of the metal/phosphorus/oxygen (M = Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Nb, Mo, Ta, W) systems.[23]. Also in cases where experiments in temperature gradients fail because of an inadequate rate of deposition or separation of the components of a polynary phase, "short-path transport" may be advantageous.

2.4. Deposition of Metastable Compounds from the Gas Phase

It may appear unlikely that *metastable* compounds can be obtained through chemical transport since the reaction is determined by equilibria [such as in Eq. (1)]. But in many cases the equilibria between the various phases possibly occuring at the sink side or between the modifications of one substance will not adjust (quickly enough) at the relatively low temperatures used. With sufficient supersaturation of the gas phase in the sink, deposition of a metastable solid phase is possible through a type of "metastable equilibrium" (see Ostwald's Rule of Stages), without these phases converting to the thermodynamically stable solid during the course of the experiment. Many examples (Nb_2O_5 modifications,[30, 31] ternary RE metallates (such as $LnTa_3O_9$ or $LnNb_7O_{19}$, see Section 7 and Table 7), tantalates and niobates of thorium (see Section 7), CoP_2 (see Section 5.3)[32]) have demonstrated that otherwise inaccessible compounds with potentially interesting new crystal structures can be obtained in this way.

2.5. Pathways to Maximum (Thermochemical) Information

Beyond their applications for preparative purposes, chemical transport reactions offer a relatively simple possibility to obtain important thermochemical information for the solids under investigation. Even if this is not the major objective of the experiment, *certain procedures* should be kept in mind when carrying out a reaction to not overlook simple accessible (thermochemical) information. For this purpose, the qualitative and quantitative composition of the equilibrium solids in the sink *and* the source, the migration rate, the order of deposition of the individual phases and, the solubility of the solids in the gas phase (from the difference between the initial and final weights) must be recorded *and* published.

In order to understand the thermodynamic causes of the reaction, one prerequisite is that the reaction is carried out under near equilibrium conditions. To get as close as possible to this state in the experiment, also in the interests of reproducibility, it is recommended that a so-called "*purification transport*" with the "reverse" temperature gradient is performed before applying the experimental temperature gradient. This can help the various heterogeneous (solid/solid, gas/solid) and homogeneous (gas/gas) equilibria to become established before migration and deposition in the sink begins. If solids with complex compositions are to be synthesized "in situ" during a transport experiment (e.g. $TiPO_4$ from $4TiO_2$, $4TiP_2O_7$, TiP[33]; $LaTaO_4$ (see Section 7)), several days of purification transports or pre-reaction may be necessary to establish the equilibria. In our experience, setting up the heterogeneous equilibrium between a single-phase solid and the gaseous transport agent takes only minutes (one hour maximum).

Information on the partial pressures that occur (partial pressure differences) can be obtained from the transport rates (TR or $\dot{m}$), if they are measured under the appropriate, carefully selected reaction conditions. However, this data can still contain considerable uncertainties. More precise thermochemical predictions can be obtained in many cases if one avoids looking solely at the desired phase ("single-phase transport") in the sink, as was recommended in earlier times,[9] but instead by assuming the presence of a multiple-phase deposit and by including the *appearance* or *disappearance of phases* in the source and the sink in the thermodynamic calculations. In this way it is possible to estimate the thermodynamic data of a previously unknown substance, for example, participating in the reaction.

To stop a transport experiment, the ampoule should always be removed from the oven with the source side first. This procedure ensures that the gas phase condenses onto the remaining starting solid and does not contaminate the phases deposited in the sink.

With the generally used method for chemical transport experiments, the transport rate is obtained as the ratio between the mass of the solid in the sink to the reaction time. With this method, with a multiple-phase solid in the sink, it is only possible to determine a *mean transport rate*. The experiment time can only be definitely determined when solid is still present on the source side of the ampoule when it is taken out of the oven (otherwise migration could have already ended much earlier, without this being recognized).

By means of a measurement arrangement developed in our research group, the so-called transport balance,[18] to follow the progress of chemical transport experiments over time, the individual observations (quantity of solids, migration rates, sequence of deposition) can be determined even on a sealed ampoule with sufficient accuracy (see Section 3). The program CVTRANS can be used to model the very detailed experimental information obtained (see Section 4).

3. The Transport Balance and the High-Temperature Gas-Phase Balance

With the conventional method of measuring the TR, despite great care when carrying out the experiments, results were obtained for several systems that were only poorly reproducible.[34] Further investigations showed that the deposition was kinetically inhibited, and could be initiated by coincidental external influences (e.g. CT of tungsten[35]). In contrast to the considerations of Schäfer[9] on the chemical transport of a single-phase solid which coexists with the gas phase only but not with other condensed phases, we were able in the past years to characterize transport systems with much more *complex migration characteristics*. For example in the transport of phosphides with iodine, metal iodides are often formed in addition to the introduced phosphides (see Section 5.3).[78, 79, 100] Multiple-phase compositions of the solid can also be observed in the transport of CuO with iodine (CuO_s, Cu_2O_s, CuI_l)[36] or with anhydrous sulfates (e.g. $FeSO_{4,s}$, $Fe_2O_{3,s}$, $Fe_2(SO_4)_{3,s}$).[124–126] A further example is the chemical transport of the various phases occurring in the Cr/O/Cl system, in particular CrOCl ($Cr_2O_{3,s}$, $CrOCl_s$, $CrCl_{2,s}$, $CrCl_{3,s}$).[37, 38] In all these examples, the *transport balance* (HTB, Figure 1) has proven very valuable when performing the experiments. This balance was constructed according to the principles of a beam balance. The migration of a solid within the ampoule (from the end of the supporting arm in the direction of the pivot) leads to a higher loading of the electronic analysis balance. The change in weight, when certain geometric conditions are maintained, corresponds to the mass deposited in the sink and can be recorded with a personal computer. A detailed description of the construction and function of the apparatus can be found in the literature.[18, 67] Figure 2 shows the example of the *progress over*

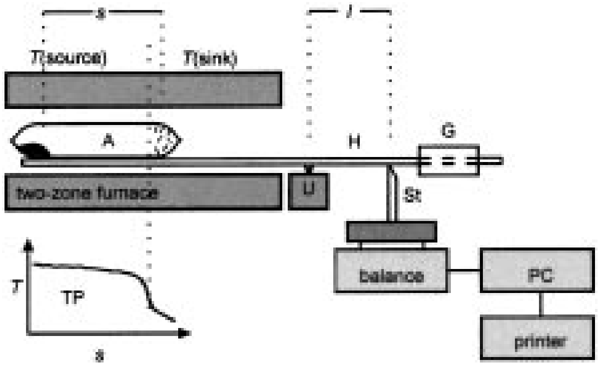


Figure 1. Schematic representation of the transport balance.[18] A: ampoule, H: balance beam made from two corundum rods, G: counter weight, St: rod for the digital balance, TP: temperature profile, U: pivot of the balance beam, *s*: transport path (diffusion path).

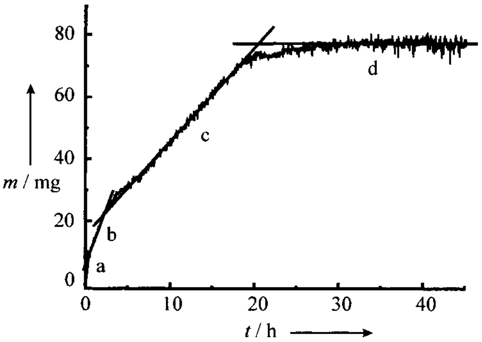


Figure 2. Measurement protocol for the chemical transport of Rh_2O_3 with chlorine.[105] a) Establishing equilibrium between the solid and the gas phase, b) sublimation of $RhCl_3$, c) transport of Rh_2O_3, d) complete transport.

time of a chemical transport experiment[105] of Rh_2O_3 with chlorine (1075 → 975 °C, 75 mg Rh_2O_3, 54 mg Cl_2, $V = 20\ cm^3$, $s = 10$ cm), as recorded with the transport balance. Once equilibrium has been established (section a in Figure 2) three sections with differing slopes (transport rates) can be seen. In section b the deposition of $RhCl_{3,s}$ ($\dot{m} \approx 8\ mg\,h^{-1}$, $m \approx 22$ mg) occurs at a higher rate, then (section c) $Rh_2O_{3,s}$ migrates ($\dot{m} \approx 3\ mg\,h^{-1}$, $m \approx 55$ mg), until the solid in the source is completely consumed (section d). The measurement arrangement enables the individual transport rates for the two steady states b and c, as well as the masses of the solids to be determined with sufficient accuracy *without* the need *to open the ampoule*. Individual experiments and also complete measurement series at variable temperature can therefore be performed with a single ampoule. In this way, very detailed and more reproducible data can be obtained than by the conventional method and evaluation of transport experiments.

The *amounts* of $RhCl_{3,s}$ observed besides $Rh_2O_{3,s}$ during the Rh_2O_3/Cl_2 experiment described agree very well with the thermodynamic calculations.[105] The $RhCl_{3,s}$ mass is obtained from Equations (2) and (3) and is essentially determined by the thermodynamic stability of the two solids. In contrast, thermodynamic conclusions (for example, about the stability of a deposit) derived from the observed transport rates, can easily be falsified by "non-thermodynamic" influences (kinetics, convection).

$$Rh_2O_{3,s} + 3\,Cl_{2,g} \rightleftharpoons 2\,RhCl_{3,s} + \tfrac{3}{2}O_{2,g} \qquad (2)$$

$$RhCl_{3,s} \rightleftharpoons RhCl_{3,g} \qquad (3)$$

An interesting modification of the "transport balance" is the "*high-temperature gas-phase balance*".[39] In this case the shift in the center of gravity of the mass of the ampoule contents (see Figure 1) is not caused by chemical transport in a temperature gradient but by simple isothermal vaporization or decomposition of the solid at one end of the ampoule. The measured loss in mass for the vaporization of potassium iodide (500 mg KI, $l = 12$ cm, $V = 24\ cm^3$) as a function of the temperature is shown in Figure 3.[40] The drop in the curve in the nonsaturation region is caused by an incomplete correction of the baseline.

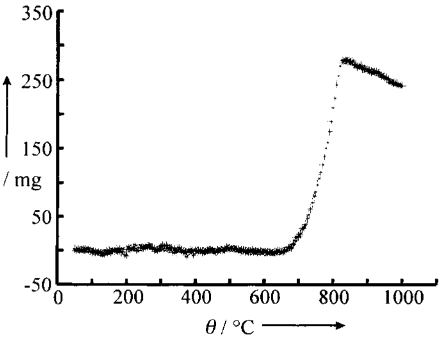


Figure 3. High-temperature gas-phase balance.[39] Vaporization of KI.[40] Start of vaporization at about 620 °C; above about 810 °C the compound is completely gaseous.

4. Thermodynamic Modeling of Chemical Transport—The Computer Program CVTRANS

A comprehensive summary of the different concepts used to describe chemical transport experiments has recently been provided by Lenz and Gruehn.[67] Therefore we will limit the description here to the models and procedures used in our research group.

4.1. Modeling Chemical Transport Experiments

Modeling chemical transport experiments has different objectives. Orientational calculations *before* an experiment can give information about the most favorable conditions with respect to temperature and the choice of transport agent. Modeling *after* an experiment, or better after a series of experiments under systematic variation of the reaction conditions, gives information about the composition of the equilibrium gas phases, which is only rarely accessible by direct measurement. It is possible, by means of a critical(!) comparison of the observations (see Section 2.5) with the results of model calculations, to check or at least delimit the thermodynamic data (TD) (enthalpies of formation of VP[78], CrP and MnP[79], niobates MNb_2O_6,[159] CrOCl,[38] anhydrous sulfates MSO_4 and $M_2(SO_4)_3$[124–126]). Overall, thermodynamic analysis leads to a very detailed understanding of the chemical equilibria occurring in such a (transport) system.

The aim of modeling is to attain an exact as possible reproduction of the different observations in a transport system. A differentiation must be made between values that depend exclusively on the thermodynamics of the participating condensed phases and gas molecules, such as the composition of the equilibrium solids and their solubility in the gas phase, and values that are influenced by "non-thermodynamic" effects or even determined by them. *Transport rates* belong to the latter category. These are connected to the partial pressure differences between the source and sink and therefore also with the thermodynamic characteristics of the system according to the diffusion formulation of Schäfer [Eq. (4)][9], but can also be considerably influenced by kinetic effects and mass flux by convection.

$$\dot{m} = \frac{a \Delta p_c}{c \sum p} \frac{\overline{T}^{0.8} q D_0}{s} 1.8 \times 10^{-3} \quad [mol\,h^{-1}] \qquad (4)$$

$\dot{m}$: Transport rate [$mol\,h^{-1}$]; a,c: stoichiometric coefficient of the transport equilibrium (for the CT of Rh_2O_3, [see Eq. (27)], $a/c = 1/2$); $\Delta p_c = p(C)_{source} - p(C)_{sink}$, where $p(C)$ is the equilibrium pressure; Σp: total pressure; $\overline{T}$: average temperature of the diffusion path [K]; q: cross-section [cm^2] and s: length [cm] of the diffusion path or the transport path; D_0: mean diffusion coefficient [$cm^2 s^{-1}$] (values between 0.1[9] and 0.025[41, 42, 49] have been reported in the literature for D_0.)

To a limited extent, the influence of convection on the transport rates can be approximated,[14] but, overall, these calculations are relatively uncertain and the underlying theories of flow dynamics have not yet been adequately developed.[67] For the further analyses given here, therefore, the validity of the formulation from Schäfer is taken as a prerequisite.

The calculation of the equilibrium solids and the gas phases in the source and sink are carried out in our method by means of the *minimization of the free enthalpy* of the system (G_{min} method).[43, 50] For this the experimental conditions (temperature, ampoule volume, initial weights) are required, as well as the thermodynamic data [$\Delta_{\mathrm{B}}H^0_{\mathrm{T}}$, S^0_{T}, and also possibly $C_p(T)$] for all the gas molecules and condensed phases under consideration. The advantage of this procedure over the better known method for the calculation of the equilibrium partial pressures via K_p is, on one hand, in the easy, prerequisite free handling of multiple-phase deposits (the occurrence of certain phases follows from their TD), and, on the other hand, in the simple automation of the calculation (see Section 4.2). In addition to the equilibrium calculations, the *cooperative transport model*[19, 44] for the calculation of experiments is of fundamental importance. The basic idea of the model is illustrated by the flow diagram in Figure 4. The first step is an equilibrium calculation (Q_1) for the source temperature. Regarding the experimental conditions and the TD this gives the equilibrium solids and the partial pressures in the source. In a second calculation step, a further equilibrium calculation (S_1) for the temperature of the sink is performed with the *composition of the equilibrium gas phase from* Q_1. One restriction must be taken into consideration: $\Sigma p_{\mathrm{source}} = \Sigma p_{\mathrm{sink}}$ must be fulfilled. From this requirement, it is unavoidable that occasionally an ampoule volume is calculated for S_1 that deviates more or less strongly from that of Q_1. Schäfer was able to show earlier that this effect does not cause problems when deriving transport rates from calculated partial pressures.[45]

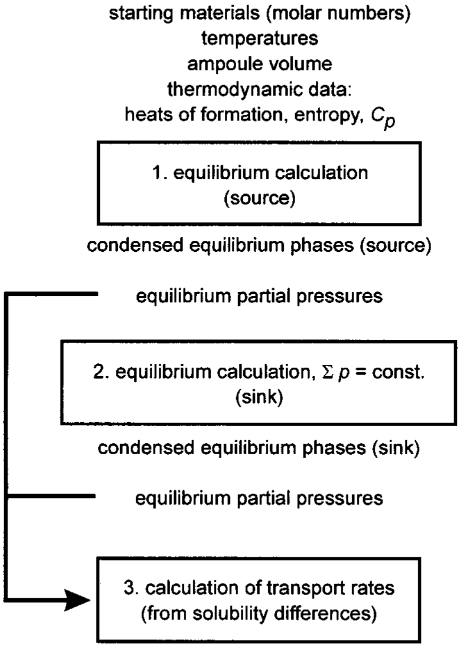


Figure 4. Cooperative transport model. See text for details.

The great advantage of the cooperative transport model over other models ("ε relationship",[13, 46] "four-stage-model"[47, 48])[67] in our experience lies in the easy handling of a transport system, in which the components of a multiple-phase equilibrium solid are transported one after another from the source to the sink; so-called *non-stationary transport behavior*. To model such experiments, a new source calculation, Q_2, follows on from S_1. This possibility was first recognized by Schmidt and used to calculate the chemical transport of GeO_2 with hydrogen (solid: $GeO_2 + Ge$, 750 → 850 °C).[49] In contrast to Q_1, the original weight is not used for Q_2, but an elemental mass balance that is obtained from the original weight minus the mass of the solid from S_1. S_2 follows on from Q_2, then Q_3, S_3, and so on. In this way the entire solid in the source is gradually shifted to the sink. In the transport of multiple-phase solids, a sequence of steady states is observed in the calculations, which means that one phase is "dissolved" in one Q_n calculation and then deposited in S_n. As long as the amount of one phase decreases in the source and increases in the sink in each calculation cycle, the composition of the gas phase from the source to the sink remains constant (steady-state behavior). The transition from deposition of one phase to the next is characterized by the non-stationary behavior of the gas phase. A concrete example (Figure 2) shows the already quoted migration of $Rh_2O_{3,s}$ after the deposition of $RhCl_{3,l}$ where the model calculations over several cycles find a dissolution of the oxide in the source but continuing deposition of the chloride in the sink. In this way, the amount of oxygen in the gas phase increases from cycle to cycle until ultimately its activity is sufficiently high to prevent further deposition of chloride in the sink. The steady-state transport of Rh_2O_3 follows this "non-stationary" region in the calculation. *It is only meaningful to report calculated transport rates* when the model calculations have been performed on the basis of partial pressures *in steady-state regions.*

4.2. The Computer Program CVTRANS

The computer program CVTRANS[21] was developed in our research group for the above-mentioned model calculations. The program was preceded by the less user-friendly programs SOLGASMIX,[50] EPCBN,[51, 52] and its derivatives EPC, EPDELT, and EPLAM[53] that were used for several years in our group. CVTRANS was developed with the programming language Delphi 2.0 for Windows 95/98. In accordance with the Windows interface, almost all the "self-explanatory" inputs are performed with several "windows" (DATA, INPUT, CALCULATION, RESULTS). Even very involved calculations with many cycles or model calculations of entire experimental series are possible in only a few minutes. In addition to the improved user friendliness, the program has several additional routines with which the iteration algorithm for the minimization of G has been improved and stabilized considerably in comparison with similar programs.

The program is available on request from the authors with additional explanations and is also accessible on the Internet.[21]

5. Metals, Intermetallic Compounds, Silicides, and Phosphides

Because of the direct technical interest, chemical transport for purification and crystallization of many elemental metals and semimetals has been the focus of extensive investigation for some time. Here we will report only on fundamental research, principally from Schäfer et al., (Si,[54, 55] Ge,[56–58] Nb,[80] Ta,[59] Mo,[60] W,[35] Fe,[61] Co, Ni,[61] Cu,[62] Ag, Au, Pt metals[63]) and review articles on this field of research.[64, 65] In particular, the gas-phase transport of molybdenum and tungsten in connection with the mode of function of halogen lamps has been repeatedly and thoroughly investigated.[66–68]

5.1. Intermetallic Phases

Despite the extensive work already done, it was only in the past few years that Binnewies and co-workers investigated the crystallization of alloys and intermetallic compounds by means of chemical transport experiments. Table 2 contains a list of the results obtained. In the systems Mo/W[69] and Co/Ni,[70] which show continuous miscibility, and Cu/Ag,[71] transport behavior similar to that of the pure metals is observed. A new feature is the occurrence of mixed gaseous halides of the metals A and B (e.g. $Cu_{3-x}Ag_xI_{3,g}$), without the thermodynamics of the vaporization of the metals being greatly altered. The germanides and stannides in the systems Cr/Ge,[72] Co/Ge,[73] Ni/Sn,[74] Ni/Ge, Co/Sn, and Cu/Sn[17] show modified transport behavior with respect to the elements (see Table 2). The available observations did not permit an extensive thermodynamic discussion of the participating transport reactions. The examples show, however, the great preparative advantage of the method for the crystallization of intermetallic phases at temperatures much lower than their melting points. It will be interesting in the future to investigate the above-mentioned and also new "intermetallic" transport systems to gain an in-depth understanding of the complex thermodynamic interactions (nonstationary transport behavior, deposition of phases with broad homogeneity ranges, and the control of their compositions).

5.2. Silicides

After the orientational research in the early 1970s (Ti_5Si_3, TiSi, $TiSi_2$, VSi_2, Cr_3Si, Cr_5Si_3, CrSi, $CrSi_2$, FeSi[75, 76]), the work of Krabbes, Oppermann and co-workers, in particular, led to a detailed thermochemical understanding of the migration of this class of substances in a temperature gradient.[77]

As examples only the heterogeneous equilibria that determine the transport of $CrSi_{2,s}$ will be discussed. With the addition of chlorine or bromine, migration to the cooler side of the ampoule is observed: it is not the halogens themselves that act as the transport agents but the halides $SiCl_{4,g}$ and $SiBr_{4,g}$ that are the result of a reaction prior to Equations (5) and (6).

$$CrSi_{2,s} + 3\,SiCl_{4,g} \rightleftharpoons CrCl_{2,g} + 5\,SiCl_{2,g} \qquad (5)$$

$$CrSi_{2,s} + 3\,SiBr_{4,g} \rightleftharpoons CrBr_{2,g} + 5\,SiBr_{2,g} \qquad (6)$$

Table 2. Intermetallic phases. Crystallization by chemical transport experiments. $T_1 \rightarrow T_2$ exothermal reaction, $T_2 \rightarrow T_1$ endothermal reaction ($T_1 < T_2$).

Compound	T [°C]	Transport agent (amount)	$\dot{m}$ [mg h^{-1}]	Comments	Ref.
Mo/W	1000 → 900	$HgBr_2$ (ca. 120 mg)		deposition of mixed crystals of variable composition at T_1	[69]
Cr(Ge)	780 → 880	I_2	ca. 0.4	transport from a two-phase region Cr(Ge)/Cr_3Ge	[72]
Cr_3Ge	780 → 880	I_2	ca. 0.4		[72]
Cr_5Ge_3	780 → 880I_2	ca. 0.02		CT of $Cr_{11}Ge_8$ alongside Cr_5Ge_3	[72]
$Cr_{11}Ge_8$	780 → 880	I_2	ca. 0.2	CT of CrGe alongside $Cr_{11}Ge_8$	[72]
CrGe	780 → 880	I_2	≈ 0.1	CT of $Cr_{11}Ge_{19}$ alongside CrGe	[72]
$Cr_{11}Ge_{19}$	780 → 880	I_2	ca.0.3	CT of Ge(Cr) alongside $Cr_{11}Ge_{19}$	[72]
Co_5Ge_3	900 → 700	I_2	ca. 4		[73]
CoGe	900 → 700	I_2		CT from the two-phase region Co_5Ge_3/CoGe ≈ 4[a]	[73]
CoSn, Co_3Sn_2	900 → 700	GaI_3		CT from the two-phase region Co(Sn)/Co_3Sn_2	[17]
Co/Ni	900 → 800	I_2/GaI_3		Co more soluble in the gas phase than Ni, use of a three-zone oven to compensate: 900 (Co) → 940 (Ni) → 800 (sink)[b]	[70]
Ni(Ge)	1000 → 800	GaI_3		CT from the two-phase region Ni(Ge)/Ni_3Ge alongside Ni_3Ge	[17]
Ni_3Ge	1100 → 1000	GaI_3			[17]
Ni_5Ge_3	900 → 800	GaI_3		CT from the two-phase region Ni_3Ge/Ni_5Ge_3	[17]
Ni_3Sn	900 → 700	I_2 (0.8 atm at 900 °C)	< 0.2		[74]
Ni_3Sn_2	900 → 700	I_2 (0.8 atm at 900 °C)	< 0.2		[74]
δ-$Cu_{41}Sn_{11}$	550 → 600	I_2		SS:[c] "$Cu_{86}Sn_{14}$"	[17]
ζ-$Cu_{10}Sn_3$	550 → 600	I_2		SS:[c] "$Cu_{75}Sn_{25}$"	[17]
Cu(Sn)	550 → 600	I_2		SS:[c] "$Cu_{91}Sn_9$"	[17]
Cu/Ag	600 → 700	I_2 (150 mg per ampoule)		transport from the two-phase region Cu(Ag)/Ag(Cu); at T_1 (source) melt of CuI/AgI; in the gas phase $Cu_{3-x}Ag_xI_3$ ($x = 1, 2, 3$)	[71]

[a] Both Co_5Ge_3 and CoGe have a remarkable phase width; the authors did not give details. [b] No details were given by the authors on the equilibrium solids at 940 °C and 900 °C. [c] Starting solid.

The transport of $CrSi_2$ with iodine, in contrast, proceeds to higher temperatures as a result of an exothermic reaction [Eq. (7)].

$$CrSi_{2,s} + 10\,I_g \rightleftharpoons CrI_{2,g} + 2\,SiI_{4,g} \qquad (7)$$

There is a clear analogy to the transport behavior of elementary silicon[54] with iodine (exothermic at low iodine amounts; endothermic at high iodine quantities with the TA $SiI_{4,g}$).

5.3. Phosphides

For several years, we have extensively investigated the chemical transport of transition metal phosphides. As shown in Table 3, in many cases the method permits very good access to well-crystallized samples (see Figure 5e (β-WP_2), 5h CoP_2, 5i: CoP_3, 5r: CrP). In addition to the great preparative advantages, transport experiments on this class of substances have enabled further development of the method (see Sections 3 and 4). Information gained from a critical comparison of all experimental observations (see Sections 2.5 and 3) with the results from thermodynamic model calculations (see Section 4) enable, in addition, a detailed (chemical) understanding of the transport-determining equilibria. In this way, careful selection of the most favorable experimental conditions for the transport of new compounds becomes possible. Our results are summarized in the following section.

In the majority of cases it is possible to *transport transition metal phosphides with iodine.* Depending on the thermodynamic stability of the phosphide and the volatile metal iodide, migration in a temperature gradient can take place by means

Table 3. Chemical transport of phosphides. $T_1 \rightarrow T_2$ exothermic reaction, $T_2 \rightarrow T_1$ endothermic reaction ($T_1 < T_2$).

Phos.-phide	T [°C]	Transport agent (amount per ampoule)	$\dot{m}$ [mg h^{-1}]	Comments	Ref.
TiP	800 → 900	I_2 (20–140 mg)	≤ 10		[22, 92]
TiP_2	650 → 700	I_2 (150 mg)	ca. 2.2	excess P suppresses TiP	[91]
ZrP	950 → 1050	I_2 (150 mg)	≤ 20	low temps lead to formation of ZrP_2	[91]
ZrP_2	850 → 900[a]		≤ 5	at T(sink) ≥ 1050 °C deposition of ZrP	[91]
VP	810 → 930	I_2 (255 mg)	ca. 22;	$VI_{2,l}$ in the source; reversal of direction of transport possible (see text)	[78]
VP_2	800 → 700	I_2 (ca. 250 mg)	≤ 10	addition of extra phosphorus (ca. 100(!) mg per ampoule) suppresses VP	[91]
VP_4	700 → 600	I_2 (ca. 300 mg)	≤ 5	addition of extra phosphorus (ca. 100(!) mg per ampoule) suppresses VP_2	[246]
NbP	850 → 950	I_2 (200 mg)	≤ 10	no transport with smaller iodine amounts	[91]
TaP	850 → 950	I_2 (ca. 200 mg)	≤ 5	no transport with smaller iodine amounts	[91]
CrP	1050 → 950	I_2 (12–137 mg)	≤ 15	$CrI_{2,l}$ as further deposit at high iodine amounts	[22, 79]
Mo_3P	1100 → 1000 or 900 → 800	$HgBr_2$ (10 and 130 mg)	≤ 10	$Mo_4P_{3,s}$ and $MoBr_{2,l}$ as additional deposits, halide only in experiments with $\bar{T}$ = 850 °C	[87]
Mo_4P_3	1050 → 950 and 900 → 800[c]	$HgBr_2$ (10–150 mg)	≤ 10		[87]
MoP	1000 → 900 1000 → 900	I_2 (200 mg) + oxygen[b] $HgBr_2$ (50 mg)	≤ 3 ca. 3	no transport without O_2	[87, 91]
MoP_2	1000 → 900	I_2 or $HgCl_2$ (ca. 200 mg) + oxygen[b]	ca. 1[d];	excess P otherwise formation of MoP	[247]
WP	1000 → 900	I_2 (200 mg) + oxygen[b]	ca. 1	no transport without O_2	[91]
WP_2	1000 → 900	I_2 (ca. 200 mg) + oxygen[b]	ca. 2	slight P excess suppresses formation of WP; large excess suppresses transport	[247]
MnP	1000 → 1100	I_2 (a few mg)	≤ 2.6	$MnI_{2,l}$ always obtained as additional phase in the source	[22, 79]
Fe_2P	1000 → 900	$HgBr_2$ (!) (100 mg)	≤ 1	FeP always as additional phase in the source; no transport with iodine	[88]
FeP	800 → 550[a]		≤ 30		[22, 98]
FeP_2	800 → 700	I_2 (50 mg)	ca. 0.5		[99]
FeP_4	700 → 600	I_2 (70 mg)	ca. 1[d]		[99]
CoP	850 → 750[a]		≤ 10	$CoI_{2,l}$ as additional deposit at higher iodine amounts	[32, 100]
CoP_2	850 → 650	I_2 (150 mg)	≤ 2	various other phases: CoP, CoP_3, and $Co_2P_4O_{12}$; large ΔT favors formation of CoP_2	[32]
CoP_3	1000 → 900	I_2 (≥ 120 mg)	≤ 5	temperature can be varied within limits; CoP (at higher temp.) and rarely CoP_2 (at lower temp.) as additional solids	[32]
Ni_5P_4	900 → 800	I_2 (≥ 150 mg)	ca. 0.8		[248]
Cu_3P	800 → 900	I_2 (34 mg)	ca. 5	formation of CuI_l at T_1; large iodine amounts lead to formation of CuP_2 alongside Cu_3P	[93]
CuP_2	a) 750 → 650 b) 730 → 630	I_2 (26–205 mg) CuI (20 mg)	≤ 8 ca. 5	always CuI_l as additional deposit; also $Cu_2P_3I_2$ at higher iodine amounts Cu_3P as additional deposit at T_2 (see text)	[93, 249] [93]
Cu_2P_7	580 → 530	P (> 170 mg), I_2 (20 mg)	ca. 0.5	CuP_2 and/or $Cu_2P_3I_2$ as additional deposit	[93, 249]

[a] Temperature and amount of iodine added can be varied over a wide range. [b] In this experiment, oxygen was introduced into the ampoules either as H_2O or by the addition of HgO or MO_3 (M = Mo, W). [c] The deposition of Mo_4P_3 at 800 °C is unusual since this phase is only thermodynamically stable above 910 °C against decomposition to Mo_3P and MoP.[87] [d] In mg d^{-1}.

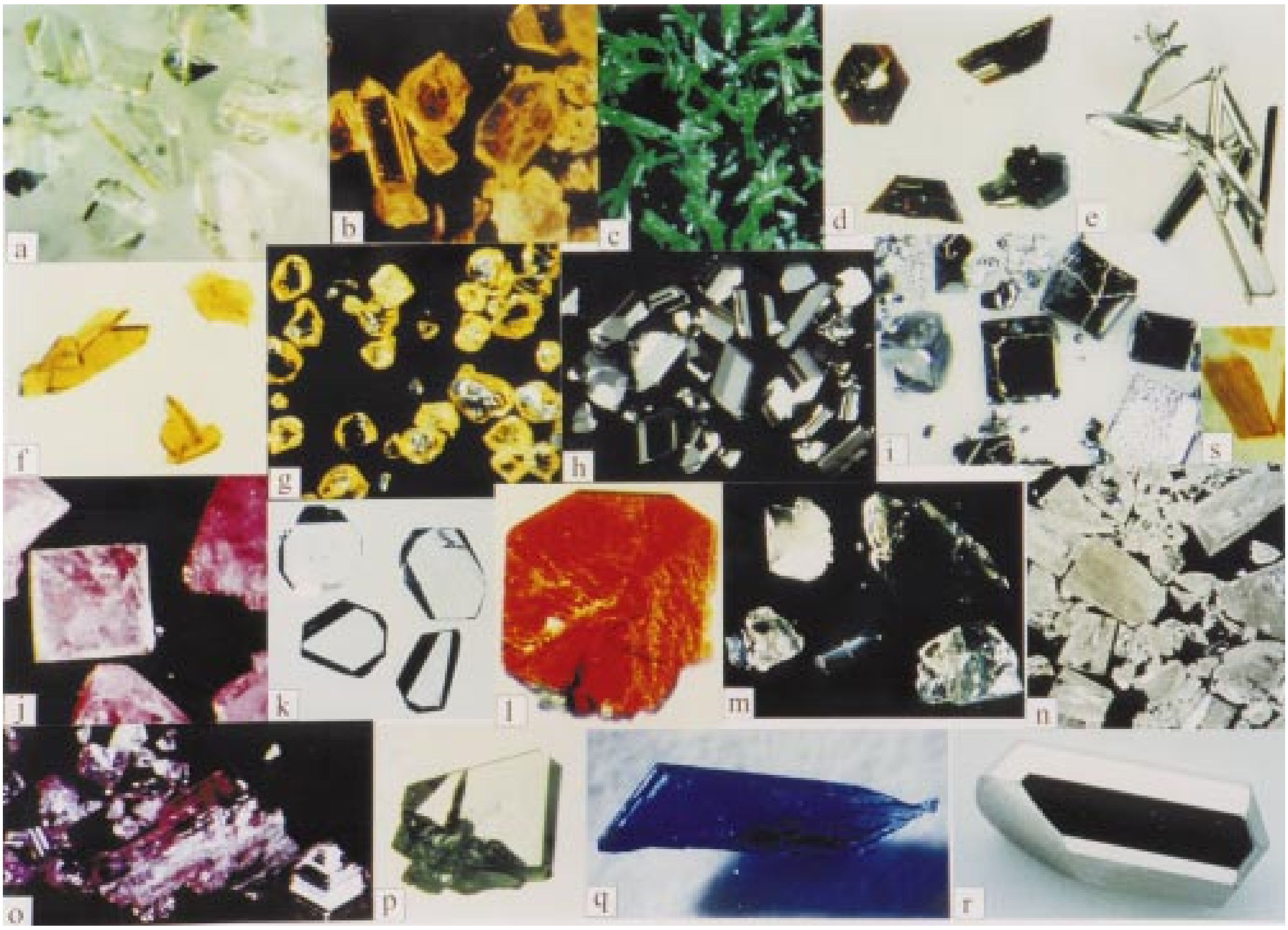


Figure 5. Crystals obtained from chemical transport experiments. a) $Yb_2Si_2O_7$ (crystal size ca. 2 mm), b) $NiSO_4$ (0.5 mm), c) $Pr_2Ti_3O_8Cl_2$ (0.3 mm), d) $RhPO_4$ (0.5 mm), e) β-WP_2 (5 mm), f) $Rh(PO_3)_3$ (0.4 mm), g) $Sm_2Ti_2O_7$ (0.3 mm), h) CoP_2 (2 mm), i) CoP_3 (2 mm), j) $NdNbO_4$ (1 mm), k) $CuSO_4$ (0.5 mm), l) $Pd_2P_2O_7$ (2 mm), m) $FeSO_4$ (1 mm), n) Ta_2O_5 (0.4 mm), o) $Nd_4Ti_9O_{24}$ (1 mm), p) CuP_4O_{11} (4 mm), q) $Cr_2P_2O_7$ (10 mm), r) CrP (8 mm), s) $Ce_2Ti_3O_8Cl_2$ (0.5 mm).

of an *exothermic* (e.g. VP/I_2,[78] MnP/I_2,[79] Cu_3P/I_2[93]) *or an endothermic* (e.g. CrP/I_2,[79] CoP/I_2,[100] CuP_2/I_2[93]) *reaction.* For the above-mentioned examples, thermodynamic model calculations resulted in the following transport-determining equilibria [Eq. (8)–(13)].

$$VP_s + 7/2\,I_{2,g} \rightleftharpoons VI_{4,g} + PI_{3,g} \tag{8}$$

$$MnP_s + 2\,HI_g \rightleftharpoons 1/2\,Mn_2I_{4,g} + 1/4\,P_{4,g} + H_{2,g} \tag{9}$$

$$Cu_3P_s + 3\,I_g \rightleftharpoons Cu_3I_{3,g} + 1/4\,P_{4,g} \tag{10}$$

$$CrP_s + I_{2,g} \rightleftharpoons 1/2\,Cr_2I_{4,g} + 1/4\,P_{4,g} \tag{11}$$

$$CoP_s + 5/2\,I_{2,g} \rightleftharpoons CoI_{2,g} + PI_{3,g} \tag{12}$$

$$CuP_{2,s} + 1/3\,PI_{3,g} \rightleftharpoons 1/3\,Cu_3I_{3,g} + 7/12\,P_{4,g} \tag{13}$$

In general, relatively large amounts of iodine of about 100 mg per ampoule are necessary for an effective transport. The failure to observe migration of NbP in earlier experiments of Schäfer[80] was due to an insufficient quantity of iodine (see Table 3).

Qualitative analysis shows that phosphides with a M:P ratio close to 1:1 apparently give the best results (high transport rates, large crystals). Migration of metal-rich or phosphorus-rich phosphides in temperature gradients, in comparison, is less effective experimentally. In addition, the transport of metal-rich phosphides ($M:P \geq 1$) of the early transition metals (Ti, Zr, V, Cr) led to the migration of the respective monophosphides and attack of the walls of the silica ampoules. Various considerations and further experimental results have made the facts understandable.

If the activity of the metal component in a phosphide is high, but that of the phosphorus very low (*metal-rich phosphide*), the only reaction is that of the TA (iodine) with the metal to form the volatile metal iodide. It is even possible that its saturation vapor pressure will be reached, so that condensed (s, l) metal halides also occur. Phosphorus becomes enriched in the solid; the simultaneous vaporization of both components of the solid is not possible. Examples for this are the reactions of $Cr_{12}P_7$ (→CrP), Fe_2P (→FeP) and Co_2P (→CoP) with iodine.[81] In an alternative but thermodynamically equally possible explanation, the failure to migrate could be caused by the occurrence of phosphorus-rich neighboring phases that limit the *phosphorus existence pressure.* The partial pressures $p(P_2)$ and $p(P_4)$ cannot attain sufficiently high values under these conditions (according to Schäfer $\geq 10^{-5}$ atm)[82] to allow a detectable transport effect. The thermodynamic stability of the phosphorus iodides $P_2I_{4,g}$ and $PI_{3,g}$[83–86] is not sufficient under such conditions to keep phosphorus in the gas phase. These considerations led to the successful use of *$HgBr_2$ as a transport agent* for Mo_3P, Mo_4P_3[87] and Fe_2P.[88] The chemical transport of the phosphorus part of these phosphides occurs in accordance with Equations (14)–(16) via the much more stable phosphorus tribromide.[87, 88]

$$Mo_3P_s + 9/2\,HgBr_{2,g} \rightleftharpoons 3\,MoBr_{2,g} + PBr_{3,g} + 9/2\,Hg_g \quad (14)$$

$$Mo_4P_{3,s} + 17/2\,HgBr_{2,g} \rightleftharpoons 4\,MoBr_{2,g} + 3\,PBr_{3,g} + 17/2\,Hg_g \quad (15)$$

$$Fe_2P_s + 7/2\,HgBr_{2,g} \rightleftharpoons 2\,FeBr_{2,g} + PBr_{3,g} + 7/2\,Hg_g \quad (16)$$

The reversal of these considerations means that, of course, the phosphorus coexistence pressure over a phosphide and its phosphorus-rich neighboring phase must be higher than about 10^{-5} atm if the former is to be transported with iodine.

The phosphorus pressure in the ampoule takes on a completely different significance in the *chemical transport of phosphorus-rich phosphides*. At temperatures that allow a sufficient vaporization of the metal component as the iodide, many phosphides with a ratio of $M{:}P < 1{:}1$ (polyphosphides) are only stable at $p(P_2,P_4) > 1$ atm. Despite the relatively low thermodynamic stability of $P_2I_{4,g}$ and $PI_{3,g}$, it is possible under such conditions that the iodine used as the TA can be bound by the phosphorus in the gas phase; it is therefore no longer available for the iodination of the metal component. For this reason, reversible chemical transport is barely possible with many polyphosphides that we know of from the work of Jeitschko[89] and von Schnering.[90] Exceptions to this are VP_4, FeP_4, and Cu_2P_7, whose metal components are particularly stable and/or form very volatile iodides, so that transport at relatively low temperatures between 500 and 600 °C with the in situ formed transport agents PI_3 and/or P_2I_4 becomes possible [Eq. (17)–(19)].

$$VP_{4,s} + 4/3\,PI_{3,g} \rightleftharpoons VI_{4,g} + 16/3\,P_{4,g} \quad (17)$$

$$FeP_{4,s} + 2/3\,PI_{3,g} \rightleftharpoons FeI_{2,g} + 14/3\,P_{4,g} \quad (18)$$

$$Cu_2P_{7,s} + 2/3\,PI_{3,g} \rightleftharpoons 2/3\,Cu_3I_{3,g} + 23/12\,P_{4,g} \quad (19)$$

The above-mentioned transport systems with phosphides show that the simple case of a single-phase solid that is identical in the source and the sink and that is present during the entire experiment is not always realized. As we have already mentioned, the reaction of a phosphide with the TA (iodine) can lead to the *formation of condensed metal iodides*. In this connection we have made an in-depth investigation of the occurrence of $VI_{2,s}$ (alongside VP)[78], $CrI_{2,l}$ (alongside CrP)[79], $MnI_{2,l}$ (alongside MnP)[79], $CoI_{2,l}$ (alongside CoP)[100] and CuI_l (alongside Cu_3P and/or CuP_2).[93] From the amount of $VI_{2,s}$, it was possible to estimate the enthalpy of formation of VP_s. In other cases it was possible to undertake a reexamination of the relative thermodynamic stability of phosphides and iodides from the mass ratios in the equilibrium solids. For such investigations, the transport balance as described in Section 3 proved to be particularly valuable.

Even if a phosphide does not have a high metal activity, the formation of very stable metal iodides (either in gaseous or condensed form), as described above, can still lead to phosphorus-rich phosphides (incongruent vaporization of the phosphides). In our experiments at sufficiently high iodine quantities, we obtained TiP_2[91] in the presence of TiP,[92] ZrP_2 in the presence of ZrP, and CuP_2 in the presence of Cu_3P (and CuI_l) [Eq. (20) and (21)].

$$2\,MP_s + 2\,I_{2,g} \rightleftharpoons MI_{4,g} + MP_{2,s} \quad (M{:}\ Ti, Zr) \quad (20)$$

$$2\,Cu_3P_s + 5/2\,I_{2,g} \rightleftharpoons 5\,CuI_l + CuP_{2,s} \quad (21)$$

The transport behavior of VP was very revealing for our understanding of the *homogeneous gas-phase equilibrium* between phosphorus and iodine in relation to pressure and temperature. This compound migrates with iodine as the transport agent as the result of an exothermic reaction [Eq. (8)]. Attempts to synthesize VP_2 (800 °C, from the elements, with iodine as mineralizer) resulted in the simultaneous occurrence of the monophosphide and diphosphide and migration of both phosphides to T_1. Under the transport conditions of $T_2 \rightarrow T_1$, $PI_{3,g}$ does not act as a phosphorus carrier as in Equation (8) or (12) but becomes the transport agent itself [Eq. (22)].

$$VP_s + 4/3\,PI_{3,g} \rightleftharpoons VI_{4,g} + 7/12\,P_{4,g} \quad (22)$$

The similarity to the transport behavior of the silicides (Section 5.2) and to that of elemental silicon[54] is clear. CuP_2 can migrate in temperature gradients both by means of exothermic reactions (in the presence of Cu_3P_s and CuI_l as deposits, low amounts of P and I in the gas phase) and by means of endothermic reactions.[93] In the latter case, CuI_l and phosphorus vapor ($P_{2,g}$, $P_{4,g}$ but also $PI_{3,g}$ and $P_2I_{4,g}$) are formed from a reaction of $CuP_{2,s}$ and added iodine that occurs prior to transport. With $PI_{3,g}$ as the TA, the vaporization of the remaining $CuP_{2,s}$ is achieved by an endothermic reaction [Eq. (23)].

$$CuP_{2,s} + 1/3\,PI_{3,g} \rightleftharpoons 1/3\,Cu_3I_{3,g} + 7/12\,P_{4,g} \quad (23)$$

But now some *experimental information*: If a temperature gradient is applied immediately after phosphides have been formed in situ from the metal and phosphorus in a silica ampoule with iodine as the mineralizer, in our experience, there is frequently only a relatively low transport effect to be observed, which is sometimes even completely absent. If, in contrast, a previously synthesized phosphide is used as the starting solid, the transport rates will be much higher and well reproducible. We think that this behavior has two causes. Traces of moisture that have been introduced together with iodine and phosphorus react with the phosphide to form phosphates with the release of hydrogen. This in turn binds the iodine required as the transport agent in the form of HI_g which is less favorable for the transport of phosphides. According to our observations, this effect[78, 100] is possible with small to intermediate iodine amounts of $m(I_2) \leq 100$ mg per ampoule. In this way the experimental transport rates can be drastically decreased in comparison to those expected for a completely dry system.

It also cannot be excluded that oxygen, which can enter the ampoule by various means (traces of moisture, slight oxidation of the metal used), has an unfavorable influence on the transport of phosphides. This appears to be particularly significant when a phosphide migrates with iodine as a result of an exothermic reaction ($T_1 \rightarrow T_2$). With the simultaneous presence of a phosphate, the phosphide is transported in a coupled transport reaction with the phosphate to the cooler side of the ampoule ($T_2 \rightarrow T_1$). Examples for such behavior are given in Section 6.3.2.

One good possibility to obtain phosphides is their *synthesis starting from the oxides.* Aluminum[94] or excess phosphorus[95] can be used as reduction agents in "one pot" reactions [e.g. Eq. (24)–(26)].

$$WO_{3,s} + 1/4\,P_{4,g} + 2\,Al_l \rightleftharpoons WP_s + Al_2O_{3,s} \quad (24)$$

$$WO_{3,s} + 1/4\,P_{4,g} \rightleftharpoons 2/5\,WP_s + 3/5\,WOPO_{4,s} \quad (25)$$

$$MO_{3,s} + 4/5\,P_{4,g} \rightleftharpoons MP_{2,s} + 3/10\,P_4O_{10,g} \qquad (M = Mo, W) \quad (26)$$

The separation of the phosphides from the other reaction products can be performed by means of chemical transport reactions.

The crystallization of CoP_2 is an example for the deposition of a *metastable* compound from the gas phase. Isothermal tempering of equimolar amounts of CoP and CoP_3 leads only in exceptional cases to the formation of small amounts of CoP_2. In contrast, with CT, larger amounts of CoP_2 in the presence of CoP and CoP_3 are formed.[96, 32] The diphosphide can be deposited in the sink as a single phase with the application of an unusually steep temperature gradient $\Delta T = 200°$.[97]

6. Binary and Multicomponent Oxides

The transport behavior of most binary oxides in temperature gradients is already well known from earlier work by Schäfer, Oppermann, and several other authors, and is summarized in review articles.[101, 102] The transport of complex oxides (sulfates, phosphates, niobates and compounds of the systems Ln/TM/O/Cl) has therefore been of interest to us more recently. It was also possible to gain some new knowledge of the chemical transport of the simple binary oxides.

6.1. Binary Oxides

The chemical transport of Cu_2O and CuO with various transport agents is possible due to the exothermic reactions that occur over wide ranges of temperature and transport agent concentration with the deposition of single-phase oxides.[62, 101, 103, 104] The chemical transport of multiple-phase solids (up to three: CuO_s, Cu_2O_s, CuI_l) and the accompanying time dependence of the transport behavior ("nonstationary behavior") can be quantitatively understood by means of experiments on the transport balance and extensive thermodynamic modeling.[36] Calculations on this model system show how precisely the transport behavior of a system can be modeled with reliable thermodynamic data.

Nonstationary behavior was also observed in the first investigation of the migration of Rh_2O_3 in temperature gradients (e.g. 1000 → 900 °C) with the TA chlorine [ca. 1 atm at room temperature (RT)].[105] Model calculations agreed well with both the experimental composition of the deposit ($Rh_2O_{3,s}$, $RhCl_{3,s}$) and also the transport rates for the two phases as a function of temperature and concentration of chlorine.[105] The equilibria (27) and (28) fully describe the behavior.

$$Rh_2O_{3,s} + 3\,Cl_{2,g} \rightleftharpoons 2\,RhCl_{3,g} + 3/2\,O_{2,g} \quad (27)$$

$$Rh_2O_{3,s} + 3\,Cl_{2,g} \rightleftharpoons 2\,RhCl_{3,s} + 3/2\,O_{2,g} \quad (28)$$

The crystallization of a further precious metal oxide under participation of the gas phase succeeded in the PdO system (e.g. 800 → 900 °C, TA: Cl_2, 1 atm at RT). The addition of $PdCl_2$, which decomposes into $Cl_{2,g}$ and Pd_s at these temperatures, also promoted the migration of the oxide in a temperature gradient as a result of an exothermic reaction.[106, 107] Thermodynamic modeling of the experimental observations was, however, not possible. Uncertainties in the thermodynamic characterization of the Pd/Cl system appeared to be responsible.[127]

In contrast to the migration and deposition of many compounds of the Ln/TM/O/Cl systems in temperature gradients (see Section 7), the chemical transport of binary La_2O_3 with chlorine is not possible. It is not the high thermodynamic stability of $La_2O_{3,s}$ in comparison to $LaCl_{3,g}$ that is responsible but rather the almost quantitative formation of very stable $LaOCl_s$ [Eq. (29)] from La_2O_3 and chlorine.[108] The chemical transport of $LaOCl_s$ with chlorine according to Equation (30) is possible, however (1150 → 1000, 0.1 atm Cl_2 at RT).[108]

$$La_2O_{3,s} + Cl_{2,g} \rightarrow 2\,LaOCl_s + 1/2\,O_{2,g} \quad (29)$$

$$LaOCl_s + Cl_{2,g} \rightleftharpoons LaCl_{3,g} + 1/2\,O_{2,g} \quad (30)$$

Despite the close chemical relationship between the rare-earth oxides and Sc_2O_3, the latter can be transported, although at relatively low rates (1 atm Cl_2 at RT; 1100 → 1000). Formation of $ScOCl_s$ under the transport conditions was not observed.[159]

In contrast to the sesquioxides Ln_2O_3, cerium dioxide does not react with the transport agent chlorine to form $CeOCl_s$, but migrates in a temperature gradient (e.g. 1100 → 1000 °C). However, the transport effect is very low as a result of the high stability of CeO_2; the strongly endothermic equilibrium [Eq. (31)], which is probably decisive, lies too far to the left.

$$CeO_{2,s} + 3/2\,Cl_{2,g} \rightleftharpoons CeCl_{3,g} + O_{2,g} \quad (31)$$

A more favorable equilibrium state with much higher transport rates can be achieved with the addition of a little carbon, which leads to the formation of CO_2 on the right-hand side.[109] The pale pink color of the almost colorless cubes of the CeO_2 crystals is probably caused by traces of Pr^{3+}.[110] With low amounts of additional Ta_2O_5, the crystals of $Ce_{1-x}Ta_xO_2$ ($x < 0.02$) obtained took on a blue color.[109] Ta_2O_5 itself migrates with CBr_4 as the TA in a temperature gradient of 900 → 1000 °C as a result of an exothermic reaction (see Figure 5n).[109]

A comparison of thermodynamic estimates with experimental results confirms that chemical transport of ZrO_2 and HfO_2 with chlorine should proceed in accordance with Equation (32).[111]

$$MO_{2,s} + 2\,Cl_{2,g} \rightleftharpoons MCl_{4,g} + O_{2,g} \qquad (M = Zr, Hf) \quad (32)$$

$TeCl_4$ can also be used as the transport agent for the two dioxides.[102] The use of $TeCl_4$ as a transport agent has generally proven favorable, particularly in the transport of oxides.[65] An extensive investigation of the transport behavior of various

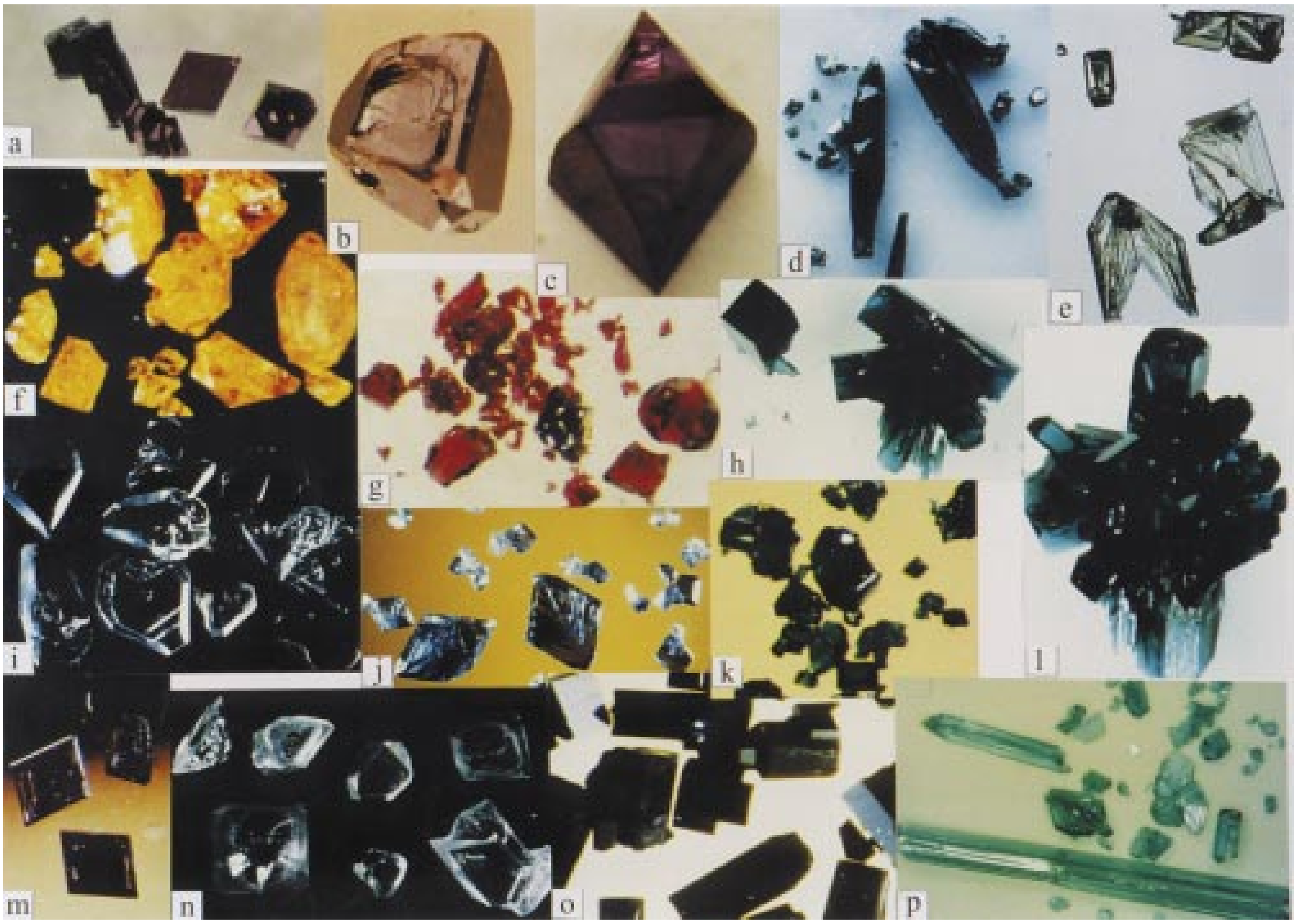


Figure 6. Crystals obtained from chemical transport experiments. a) Mo_4O_{11} (crystal size ca. 3 mm), b) WO_2 (8 mm), c) Mo_4O_{11} (10 mm), d) $TiPO_4$ (3 mm), e) $Fe_2(SO_4)_3$ (1 mm), f) σ-$Ni_2P_2O_7$ (1 mm), g) $Co_2P_2O_7$ (0.5 mm), h) $VOSO_4$ (3 mm), i) $ZnSO_4$ (1 mm), j) $Ti(PO_3)_3$ (0.5 mm), k) $Cr_2(SO_4)_3$ (0.2 mm), l) $VOSO_4$ (3 mm), m) Mo_4O_{11} (3 mm), n) $PbSO_4$ (1 mm), o) K_xWO_3 (hexagonal tungsten bronze; 1 mm), p) $Cu_2P_2O_7$ (2 mm)

Magnéli phases Ti_nO_{2n-1} with the addition of $TeCl_4$ showed, however, that HCl rather than $TeCl_4$ was the true TA.[112] The HCl is formed from the hydrolysis of $TeCl_4$ by traces of moisture, which are almost unavoidable when working with silica ampoules.[113] WO_2 (Figure 6b) shows unusually high transport rates with added $HgBr_2$ ($\sim 1000\ mg\,h^{-1}$).[67, 114] $HgBr_2$ is also suitable as a TA for Mo_4O_{11} (Figure 6a, c, m).[115]

Crystals (Figure 6o) of the hexagonal tungsten bronze (HTB) K_xWO_3 were obtained from an unexpected transport reaction with the addition of KBr to WO_3.[116]

The intensive examination of the transport behavior of the sesquioxides Cr_2O_3 and V_2O_3 with added chlorine eventually led to the detection of the gas molecules $CrOCl_{2,g}$ and $VOCl_{2,g}$.[117, 118] Extensive experimental studies and subsequent thermodynamic analysis enabled the influence of these molecules on the chemical transport of $CrOCl_s$ and $V_2O_{3,s}$ to be described quantitatively. The vaporization of CrOCl in the presence of small amounts of chlorine follows Equation (33),[119] whereas for V_2O_3, Equation (34) applies for the transport after almost quantitative reaction with the chlorine.[120]

$$CrOCl_s + 1/2\,Cl_2 \rightleftharpoons CrOCl_{2,g} \qquad (33)$$

$$V_2O_{3,s} + 2\,VOCl_{3,g} + VCl_{4,g} \rightleftharpoons 5\,VOCl_{2,g} \qquad (34)$$

6.2. Sulfates

The crystallization of anhydrous sulfates has long presented a challenge. Most representatives of this class of compounds have a relatively low thermal stability. It is not usually possible to melt the compounds without the loss of $SO_{3,g}$ (or $SO_{2,g}/O_{2,g}$) under normal laboratory conditions. Since crystallization from solution (conc. H_2SO_4) can only be performed for a few anhydrous sulfates, crystallization procedures for these compounds were generally lacking. The use of chemical transport experiments for crystal growth through the gas phase has led to remarkable progress in this field. As shown in Table 4, the range of successfully transported sulfates extends from Ag_2SO_4[121] to $VOSO_4$[122] and includes many MSO_4 and $M_2(SO_4)_3$ compounds. In addition to the great preparative advantages, the in-depth investigations into the transport behavior of sulfates also yielded extensive information on the transport of heterogeneous (solid/gaseous) and homogeneous (gas phase) equilibria. It was shown that *several* transport reactions must often be taken into account for a quantitative description of the transport behavior. This requirement places particular demands on the thermochemical description of the experimental observations. This information takes on an even greater importance

Table 4. Anhydrous sulfates. In all cases, chemical transport occurs as a result of endothermal reaction with the respective transport medium.

Sulfate	Temperatures [°C]	Transport agent	$\dot{m}$ [mg h^{-1}]	Comments	Ref.
Ag_2SO_4	$800 \rightarrow T_1$	Cl_2		$AgCl_l$ forms alongside the sulfate; formation of a low-melting eutectic mixture; $T_1 < 680\,°C$ (m.p. Ag_2SO_4)	[121]
$BeSO_4$	$700 \rightarrow 600$	Cl_2 (1 atm at RT)	ca. 1[a]	mixture of $BeSO_4$/BeO as starting material	[250]
$MgSO_4$	$800 \rightarrow 700$	Cl_2 (1 atm at RT)	ca. 2[a]		[250]
$SnSO_4$			no transport		[121]
$PbSO_4$	$830 \rightarrow 730$	Cl_2 or HCl (1 atm at RT), $HgCl_2$ or I_2 (ca. 200 mg per ampoule)	≤ 50		[18, 121]
$MnSO_4$	$840 \rightarrow 740$	Cl_2 or HCl (1 atm at RT)		moderate transport rates	[121]
$FeSO_4$	$650 \rightarrow 550$	NH_4Cl (20 mg per ampoule)	ca. 0.5	Fe_2O_3[b] at T_2	[124]
$CoSO_4$	$650 \rightarrow 550$	Cl_2 or HCl (1atm at RT)	≤ 20	formation of $CoCl_{2,l}$ alongside the sulfate	[121]
$NiSO_4$	$675 \rightarrow 560$	Cl_2 or HCl (1 atm at RT)	≤ 10	no formation of $NiCl_{2,l}$ alongside the sulfate[c]	[18, 121]
$CuSO_4$	$700 \rightarrow 600$	various TA (Cl_2, HCl, NH_4Cl, $HgCl_2$, I_2)	≤ 10	formation of $CuCl_l$ alongside the sulfate[c]	[121, 251]
Cu_2OSO_4	$750 \rightarrow 650$	$HgCl_2$ (40 mg per ampoule)	≤ 10		[251]
$ZnSO_4$	$T_2 \rightarrow T_1$	Cl_2 (1 atm at RT)	≤ 20[c]	$T_1 < 690\,°C$: N-$ZnSO_4$, $T_1 > 690\,°C$: H-$ZnSO_4$; $\Delta T = 70°$; $ZnCl_{2,l}$ alongside the sulfate	[20, 121]
$Zn_3O(SO_4)_2$	$710 \rightarrow 620$	$PbCl_2$ (ca. 5 mg per ampoule)	≤ 10		[123]
$CdSO_4$	$840 \rightarrow 740$	Cl_2 or HCl (1 atm at RT)	≤ 40	$CdCl_2$ as additional deposit	[121]
$HgSO_4$	$550 \rightarrow 470$	Cl_2 or HCl (1 atm at RT)	≤ 20	$HgCl_2$ as additional deposit, dissociative sublimation also possible	[121]
$Al_2(SO_4)_3$	$625 \rightarrow 525$	$SOCl_2$ (100 mg per ampoule)	ca. 1	other TAs (Cl_2, HCl etc.) give no transport effect[c]	[126]
$Ga_2(SO_4)_3$	$625 \rightarrow 575$	Cl_2 or HCl	≤ 20[b,d]	Ga_2O_3 at T_2	[252, 253]
$In_2(SO_4)_3$	$625 \rightarrow 575$	Cl_2 or HCl	≤ 20[b,d]	In_2O_3 at T_2	[253, 254]
$Cr_2(SO_4)_3$	$690 \rightarrow 630$	Cl_2 or HCl	≤ 80[b,d]	Cr_2O_3 at T_2	[255, 256]
$Fe_2(SO_4)_3$	$775 \rightarrow 675$	Cl_2 (1 atm at RT)	≤ 10	Fe_2O_3[b,d] at T_2	[124, 125]
$VOSO_4$	$525 \rightarrow 425$	Cl_2 (1 atm at RT)	ca. 5	V_2O_5 alongside $VOSO_4$ at higher temperatures	[122]
	$550 \rightarrow 450$	HCl (1 atm at RT)	ca. 10	V_2O_5 alongside $VOSO_4$ at higher temperatures	[122]

[a] In mg d^{-1}. [b] The amount of the oxide grows with increased temperature. [c] Transport with the addition of $PbCl_2$ also gives good results. [d] Extensive thermodynamics discussion.

since it has model character for the CT of other complex oxides with a volatile component (phosphates, arsenates, borates).

Suitable transport agents for sulfates are chlorine and HCl, as the overview in Table 4 shows. In individual cases, migration in a temperature gradient has also been observed with the addition of I_2, NH_4Cl, $HgCl_2$, $PbCl_2$, $PbBr_2$, or $SOCl_2$. The migration of sulfates always occurs by an endothermic reaction ($T_2 \rightarrow T_1$). Equations (35)–(37) fully describe the experimental observations for the transport of $ZnSO_4$ with chlorine (Figure 6i).

$$ZnSO_{4,s} + Cl_{2,g} \rightleftharpoons ZnCl_{2,g} + SO_{3,g} + 1/2\,O_{2,g} \quad (35)$$

$$3\,ZnSO_{4,s} \rightleftharpoons Zn_3O(SO_4)_{2,s} + SO_{3,g} \quad (36)$$

$$SO_{2,g} + 1/2\,O_{2,g} \rightleftharpoons SO_{3,g} \quad (37)$$

A noteworthy consequence of the interaction of Equations (35) und (36) is the much higher thermal stability of $ZnSO_4$ in the presence of chlorine.[20, 123] This effect is less pronounced when HCl is used. After extensive thermodynamic modeling, Equations (38) and (39) were shown to describe the transport of $Fe_2(SO_4)_3$ with chlorine (Figure 6e) at low temperatures (500–600 °C)

$$Fe_2(SO_4)_{3,s} + 3\,Cl_{2,g} \rightleftharpoons 2\,FeCl_{3,g} + 3\,SO_{3,g} + 3/2\,O_{2,g} \quad (38)$$

$$Fe_2(SO_4)_{3,s} + 3\,Cl_{2,g} \rightleftharpoons 2\,FeCl_{3,g} + 3\,SO_{2,g} + 3\,O_{2,g} \quad (39)$$

At higher temperatures (600–750 °C), Equation (38) no longer applies. Calculations show that under these conditions $p(SO_3)$ becomes a function of the temperature according to the (exothermic) homogeneous equilibrium in Equation (37). The oxidizing character of the equilibrium gas phase in the transport of sulfates, even when HCl is used as the TA, can be expressed in various ways. For example, in the CT of $FeSO_4$ with HCl (Figure 5m), Fe_2O_3 is always present as additional solid [Eq. (40)]. If an equivalent amount of NH_4Cl is used instead of HCl, which decomposes to form HCl, N_2, and H_2, the amount of Fe_2O_3 even increases [Eq. (41)]. Please refer to the literature for an extensive thermodynamic discussion of the transport behavior of iron sulfate.[124, 125]

$$2\,FeSO_{4,s} \rightleftharpoons Fe_2O_{3,s} + SO_{3,g} + SO_{2,g} \quad (40)$$

$$2\,FeSO_{4,s} + H_{2,g} \rightleftharpoons Fe_2O_{3,s} + 2\,SO_{2,g} + H_2O_g \quad (41)$$

An oxidizing equilibrium gas phase is also the prerequisite for the use of *$PbCl_2$ as the transport agent* for several anhydrous sulfates [$NiSO_4$, $CuSO_4$[18] (Figure 5k)]. Chlorine is released in a pre-reaction (e.g. between $NiSO_4$ and $PbCl_2$) [Eq. (42)], which involves a "double transformation" and a redox reaction. The chlorine then acts as the true TA for $NiSO_4$ [Eq. (43)].

$$2\,NiSO_{4,s} + PbCl_{2,l} \rightleftharpoons PbSO_{4,s} + 2\,NiO_s + SO_{2,g} + Cl_{2,g} \quad (42)$$

$$NiSO_{4,s} + Cl_{2,g} \rightleftharpoons NiCl_{2,g} + SO_{3,g} + 1/2\,O_{2,g} \quad (43)$$

With the transport balance, it was possible to detect the three equilibrium solids ($PbSO_4$, $NiSO_4$, NiO). It could also be shown that $PbSO_4$ (Figure 6n) migrates before $NiSO_4$ (Figure 5b) in a temperature gradient (850 → 750 °C), while NiO remained in the source at the end of the experiment.[18]

It is not possible to vaporize aluminum oxide with chlorine (or other TAs) in a temperature gradient because of the very unfavorable position of the equilibrium [Eq. (44)]. It was therefore all the more surprising that the crystallization of aluminum sulfate, $Al_2(SO_4)_3$, succeeded by means of CT (625 → 525 °C, ca. 50 mg $SOCl_2$ per ampoule, $\dot{m} \approx 0.6\ \mathrm{mg\,h^{-1}}$). The use of $SOCl_2$ as the TA apparently suppressed the formation of free oxygen and thus enabled a favorable positioning of the heterogeneous transport equilibrium [Eq. (45)].[126]

$$Al_2O_{3,s} + 3\,Cl_{2,g} \rightleftharpoons 2\,AlCl_{3,g} + 3/2\,O_{2,g} \qquad (44)$$

$(K_{P,1000\mathrm{K}} = 1 \times 10^{-10})$

$$Al_2(SO_4)_{3,s} + 3\,SOCl_{2,g} \rightleftharpoons 2\,AlCl_{3,g} + 6\,SO_{2,g} \qquad (45)$$

It has not yet been possible to establish whether the transport of rare-earth sulfates would succeed in a similar fashion. See Table 4 for information on $Cr_2(SO_4)_3$ (Figure 6k), $Ga_2(SO_4)_3$, and $In_2(SO_4)_3$.

Particular mention is made of the possibility of crystallizing $VOSO_4$ (Figure 6h and 6l) by means of CT at the end of this section. Chlorine has proven valuable as a TA [Eq. (46)].[122]

$$2\,VOSO_{4,s} + 3\,Cl_{2,g} \rightleftharpoons 2\,VOCl_{3,g} + 2\,SO_{3,g} + O_{2,g} \qquad (46)$$

In temperature gradients of 525 → 425 °C, only $VOSO_4$ occurs as a solid in the source and sink, the TRs lie around ca. $5\ \mathrm{mg\,h^{-1}}$ and increase considerably with higher temperatures (700 → 600 °C). Then, however, considerable amounts of V_2O_5 are produced in addition to the oxysulfate.[122]

6.3. Phosphates

The overview in Table 5 shows the broad applicability of chemical transport reactions for the synthesis, crystallization, and purification of this class of substances. The preparative possibilities are illustrated by the thermally labile $Pd_2P_2O_7$ (Figure 5l),[127] $RhPO_4$ (Figure 5d),[128]and $Rh(PO_3)_3$ (Figure 5f), [127] several low-melting ultraphosphates (e.g. CuP_4O_{11} (Figure 5p),[129] ZnP_4O_{11},[130]) and an series of transition metal phosphates in otherwise difficult accessible (low) oxidation states (e.g. $TiPO_4$ (Figure 6d),[33] $Ti(PO_3)_3$ (Figure 6j),[33, 141] $V_2O(PO_4)$,[131] $Cr_3(PO_4)_2$,[132] $Cr_2P_2O_7$ (Figure 5q)[133]). In addition to the elemental halogens (Cl_2, Br_2, I_2), halogen compounds (NH_4X and HgX_2; X = Cl, Br, I), and mixtures P/X (X = Cl, Br, I) were used. In the case of UP_2O_7, the chlorides VCl_4, $ZrCl_4$, $HfCl_4$, and $NbCl_5$ also proved to be suitable transport agents.[134] The best results with respect to transport rate and crystal size of the anhydrous phosphates were achieved, however, with chlorine or mixtures of phosphorus and iodine as transport agents.[23] See Table 5 for information on $Co_2P_2O_7$ (Figure 6g), σ-$Ni_2P_2O_7$ (Figure 6f), and $Cu_2P_2O_7$ (Figure 6p).

6.3.1. *Chlorine as the Transport Agent*

When chlorine is added, $P_4O_{10,g}$ is regarded as the phosphorus-carrying gas molecule, in accordance with the chemical transport of sulfates [Eq. (35), (38), and (43)]. One example is the equilibrium [Eq. (47)] that determines the transport of $RhPO_4$.

$$2\,RhPO_{4,s} + 3\,Cl_{2,g} \rightleftharpoons 2\,RhCl_{3,g} + 1/2\,P_4O_{10,g} + 3/2\,O_{2,g} \qquad (47)$$

Thermodynamic analysis of the homogeneous gas-phase equilibrium (48) shows that a notable contribution of phosphorus oxychlorides such as $POCl_{3,g}$ (or PO_2Cl,[135] or polymers of these $(PO_2Cl)_x$[136]) to the transport of phosphates is unlikely.[23] From the thermodynamic data from Equation (48), a value of $p(P_4O_{10}){:}p(POCl_3) = 278$ (1273 K, $p(P_4O_{10}) = p(Cl_2) = 1$ atm) is obtained.

$$P_4O_{10,g} + 6\,Cl_{2,g} \rightleftharpoons 4\,POCl_{3,g} + 3\,O_{2,g} \qquad (48)$$

$\Delta_R H(1273\ \mathrm{K}) = 159.2\ \mathrm{kcal\,mol^{-1}}$; $\Delta_R S(1273\ \mathrm{K}) = 44.3\ \mathrm{cal\,mol^{-1}\,K^{-1}}$;
$\Delta_R G(1273\ \mathrm{K}) = 102.8\ \mathrm{kcal\,mol^{-1}}$; $K_P(1273\ \mathrm{K}) = 2.0 \times 10^{-18}$

6.3.2. *Halogens together with Reducing Additives as Transport Agents*

As a result of the decreased activity of the metal oxide component in a phosphate, compared with the pure oxides, lower solubility of the phosphates in a chlorine atmosphere is observed. Heterogeneous equilibria such as in Equation (47) tend to lie far over to the side of the reactant and usually lead to low transport rates $\dot{m} < 1\ \mathrm{mg\,h^{-1}}$.

For this reason Schäfer and Orlovskii used mixtures of P/Cl or P/Br as transport agents for $LnPO_4$ (Ln = La, Ce, Pr, Nd).[137, 168] The release of oxygen was suppressed [Eq. (47)], which resulted in a more favorable equilibrium position [see also the CT of $Al_2(SO_4)_3$ with $SOCl_2$, Eq. (45)]. In our own investigations on transition metal phosphates with P/Cl or P/Br mixtures as TAs, we observed migration of the phosphates through the gas phase[22] but at the same time the wall of the silica ampoules was very strongly attacked with the formation of various *silicophosphates* such as $M_2Si(P_2O_7)_2$ (M^{2+} = Mn, Fe, Co,[138] Ni, Cu, Cd[139]), $M_4P_6Si_2O_{25}$ (M^{3+} = Ti, V, Cr, Mo, Fe),[22, 140, 141] MP_3SiO_{11} (M^{3+} = Ti, Cr, Mo),[141] and $MP_3Si_2O_{13}$ (M^{3+} = Ti, Cr, Rh)[81]. In general these experiments were very difficult to reproduce and were not suitable for systematic investigations. It appears that the halogenating effect of the gas mixtures of P/Cl or P/Br is so high that SiO_2 becomes soluble in the gas phase along with the phosphorus-containing solid. The search for a "*selectively*" *halogenating transport agent* for phosphates finally led to the combination of *iodine with small amounts of metal, phosphorus, or phosphide.*[22, 23] Iodine without additives as the TA only leads in exceptional cases ($TiPO_4$,[33] $Cr_2P_2O_7$[133]) to a transport effect. Equilibria such as that formulated in Equation (49) for the CT of orthophosphates require oxidation of O^{2-} by I_2 that is not very meaningful from a chemical viewpoint and are obviously thermochemically very unfavorable.

$$M_{3/n}{}^{n+}PO_{4,s}{}^{3-} + 3/2\,I_{2,g} \not\longrightarrow 3/n\,MI_{n,g} + 1/4\,P_4O_{10,g} + 3/4\,O_{2,g} \qquad (49)$$

Table 5. Anhydrous phosphates. Representative selection of the more than 60 compounds that have been crystallized through the gas phase. $\overline{T} = (T_2 + T_1)/2$.

Phosphate	Transport agent	T [°C]	Comments	Appl.[a]	Ref.
diphosphates $M_2P_2O_7$ and MP_2O_7					
$Mg_2P_2O_7$	P/I mix	$850 \leq \overline{T} \leq 1000$		+	[133, 146]
$Cr_2P_2O_7$	I_2 or I_2 + a few mg CrP	1050 → 950		+++	[22, 23, 133]
$Mn_2P_2O_7$	P/I mix	$750 \leq \overline{T} \leq 1050$		+++	[146]
$Fe_2P_2O_7$	I_2 + a few mg FeP	900 → 800		++	[133]
$Co_2P_2O_7$	a) Cl_2 (1 atm at RT) b) P/I mix	1100 → 1000 1000 → 900		+++	[97, 133]
σ-$Ni_2P_2O_7$	I_2 + a few mg Ni_5P_4	950 → 850		+++	[248]
$Cu_2P_2O_7$	I_2 + a few mg CuP_2	1000 → 900		++	[133]
$Zn_2P_2O_7$	a) H_2 (0.2 atm at RT) b) NH_4Cl (ca. 10 mg per ampoule)	920 → 820 920 → 820		++	[133, 257]
GeP_2O_7 (triclinic)	Cl_2 (0.1 atm at RT)	$700 \leq \overline{T} \leq 1000$		+	[258]
GeP_2O_7 (cubic)	Cl_2 (0.1 atm at RT)	1140 → 1050			
SnP_2O_7	Cl_2 (0.1 atm at RT)	980 → 840		+++	[259]
TiP_2O_7	a) P/I mix b) I_2 + a few mg TiP	1000 → 900 1000 → 900	$Ti(PO_3)_3$ forms with addition of excess P	+++	[33]
phosphates with transition metals in low oxidation states					
$TiPO_4$	I_2	1000 → 900	addition of a few mg Ti suppresses the formation of TiP_2O_7 alongside $TiPO_4$	+++	[33, 260]
$V_2O(PO_4)$	I_2 + a few mg V	1000 → 900		+++	[131]
$Nb_2(PO_4)_3$	I_2	800 → 700	reactants: $NbOPO_4$ + P (2:1); source: NbP, sink: $Nb_2(PO_4)_3$ and $NbOPO_4$	+++	[261, 262]
$Cr_3(PO_4)_2$	I_2 (in presence of CrP)	1200 → 1150		++	[132]
transport experiments with chlorine					
α-$CrPO_4$	Cl_2 (0.1 atm at RT)	1100 → 1000		+	[263]
$FePO_4$	Cl_2	1100 → 1000		+	[22, 23]
$RhPO_4$	Cl_2 (1 atm at RT)	1050 → 950		+	[128]
$Pd_2P_2O_7$	Cl_2 (low pressure suppresses $PdCl_2$ in the presence of the phosphate)	950 → 850		+	[127]
$Pd(PO_3)_2$	Cl_2 (low pressure suppresses $PdCl_2$)	850 → 800		–	[127]
$Hg_2P_2O_7$	PCl_5 (ca. 20 mg per ampoule)	550 → 500		+	[264]
miscellaneous phosphates					
$Ti_5O_4(PO_4)_4$	Cl_2 (1 atm at RT, addition of ca. 30 mg $TiPO_4$ per ampoule)	1000 → 900		+	[265, 266]
$NbOPO_4$ and $NbPO_{5-\delta}$	a) NH_4Cl in the presence of NbP b) I_2 in the presence of NbP, 1000 → 900, many days of purification transport favors the formation of $NbPO_{5-\delta}$	1000 → 900		+++	[262]
WP_2O_7	I_2	1000 → 900	in situ synthesis from WO_3 and P (W:P = 1:2), WP as a side product	+++	[95]
$WOPO_4$	I_2	1000 → 900	in situ synthesis of WO_3 and P (W:P = 1:1), WP as a side product	+++	[95]
MPTB[b]	$m = 4$: I_2 $m = 6$: NH_4Cl (ca. 20 mg per ampoule)	900 → 800 900 → 800		++	[95, 148]
$Mn_3(PO_4)_2$	I_2 + a few mg P	850 → 800		++	[146]
ultraphosphates					
CuP_4O_{11}	I_2 + a few mg P or CuP_2	600 → 500		+++	[93, 129]
ZnP_4O_{11}	I_2 + a few mg P or ZnP_2	600 → 500		+++	[130]
CdP_4O_{11}	I_2 + a few mg P	510 → 480		+++	[130]

[a] The column "Appl." classifies the experiments according to their preparative applicability: + + +: reversible transport without attack of the ampoule wall, transport rates $\dot{m} > 10\ \mathrm{mg\,h^{-1}}$, well-formed crystals; –: $\dot{m} < 1\ \mathrm{mg\,h^{-1}}$, reaction with the ampoule wall, bad reproducibility. + +, + and - used as gradations. [b] MPTB: monophosphate tungsten bronzes $(WO_3)_{2m}(PO_2)_4$.

The great preparative advantage of iodine in combination with reducing additives as the TA (see Table 5) provokes the question of the determining *heterogeneous and homogeneous equilibria* under these experimental conditions. In particular, it is unclear which phosphate-containing gas molecule participates in the transport.

In addition to $P_4O_{10,g}$ and $P_4O_{6,g}$, PO_g, $PO_{2,g}$, and $P_4O_{n,g}$ ($7 \leq n \leq 9$) are also known as gaseous phosphorus oxides.[142] Apart from P_4O_{10},[143, 144] the thermal behavior of phosphorus oxides is generally insufficiently characterized; data for the enthalpy of formation of $P_4O_{6,g}$ range from -380 to $-512\ \mathrm{kcal\,mol^{-1}}$.[144, 145] The thermodynamic stability of the gaseous phosphorus iodides PI_3 and P_2I_4 has already been discussed in connection with the transport of phosphides (Section 5.3).

With $PI_{3,g}$ as the transport agent and by assuming that migration of the phosphate takes place via P_4O_{10} or P_4O_6, the equilibria [Eq. (50) and (51)] are formulated for the migration of $Mn_2P_2O_7$ as an example. Similar equilibria with other lower phosphorus oxides also appear to be possible. In addition, transport with HI as the transport agent, which can be produced from phosphorus vapor, iodine, and traces of moisture, seems possible too [Eq. (52)].

$$Mn_2P_2O_{7,s} + 4/5\,PI_{3,g} + 4/5\,I_{2,g} \rightleftharpoons 2\,MnI_{2,g} + 7/10\,P_4O_{10,g} \tag{50}$$

$$Mn_2P_2O_{7,s} + 8/3\,PI_{3,g} \rightleftharpoons 2\,MnI_{2,g} + 7/6\,P_4O_{6,g} + 2\,I_{2,g} \tag{51}$$

$$Mn_2P_2O_{7,s} + 4\,HI_g \rightleftharpoons 2\,MnI_{2,g} + 1/2\,P_4O_{10,g} + 2\,H_2O_g \tag{52}$$

A direct "in situ" investigation of the gas phase (MS, IR, Raman) is hardly possible because of the comparatively high pressures and temperatures involved. Thermodynamic calculations to model the behavior of phosphates in chemical transport experiments also fail to yield conclusive proof.[33, 146] For this reason it is only possible to summarize a few observations that give information on the most important *phosphorus-containing gas molecules.*

It appears the transport of anhydrous phosphates with iodine is only possible when the partial pressure of oxygen is not "low". This can be achieved experimentally by the addition of small amounts (<10 mg per ampoule) of phosphides, metal, or phosphorus. With the exceptions mentioned above ($TiPO_4$, $Cr_2P_2O_7$), the reducing effect of the compound itself is sufficient for transport with iodine to be effective. In this connection, it is worth mentioning that the related phosphates VPO_4 and $Fe_2P_2O_7$ cannot be transported with iodine alone but only with addition of the respective monophosphides.[22] It is not possible to show quantitatively whether the oxygen partial pressure is always so low in the transport of phosphates with iodine and reducing additives that only low phosphorus oxides are present in the gas phase instead of P_4O_{10}. In several cases at least, migration is possible under conditions which do not permit a sizable P_4O_{10} pressure. For example, $Mn_3(PO_4)_2$ migrates with the transport agent mixture of P/I in a temperature gradient of $850 \rightarrow 800\,^\circ C$.[146] The next highest phosphate, $Mn_2P_2O_7$, which decomposes to the orthophosphate, thus determining the P_4O_{10} coexistence pressure, is stable up to its melting point of about 1200 °C.[147] In view of this fact it appears very unlikely that $P_4O_{10,g}$ can function as the essential molecule [$p(P_4O_{10}) \geq 10^{-5}$ atm] under the transport conditions for $Mn_3(PO_4)_2$. The same applies to the transport of TiO_2 in the presence of $TiPO_4$ ($1000 \rightarrow 900\,^\circ C$, TA: P/I) in which the *lower phosphorus oxides* should be considered as *the carriers of oxygen* and phosphorus.[33] In addition to these two examples, it can be shown for series of further phosphates in Table 5 by means of model calculations that no heterogeneous equilibria can be formulated with $P_4O_{10,g}$ as the essential phosphorus and oxygen carrier in the gas phase that would explain the observed transport effects.[23]

If the observed transport of anhydrous phosphates with iodine and reducing additives does not proceed via $P_4O_{10,g}$, the question naturally arises as to which lower phosphorus oxide does take on the dominating role. Observations of the transport of $Cr_2P_2O_7$ with iodine ($1050 \rightarrow 950\,^\circ C$) in the presence of an excess of CrP are just as noteworthy in this respect as the transport of $WOPO_4$ or WP_2O_7 in the presence of WP.[148] In all three cases, *simultaneous transport* of phosphide and phosphate was observed experimentally. In experiments with the transport balance (see Section 3) it was shown that phosphide and phosphate only migrate in a single steady state from the source to the sink when the two condensed phases are present in a particular molar ratio. If there is more phosphide present in the starting solid, the excess is transported as a second steady state to the sink. This behavior implies a *coupled transport reaction* for the two phases. It is surprising with such a complex gas-phase composition that the experimental ratio of phosphide to phosphate in all three cases agrees very well with the respective calculated ratios which were determined from the assumption of $P_4O_{6,g}$ as the transport-determining molecule in the heterogeneous equilibria [Eq. (53)–(55)]. The formulation of $WO_2I_{2,g}$ and $CrI_{2,g}$ as essential metal-carrying molecules is in agreement with many other studies.[68, 79, 149]

$$Cr_2P_2O_{7,s} + 8/3\,CrP_s + 14/3\,I_{2,g} \rightleftharpoons 14/3\,CrI_{2,g} + 7/6\,P_4O_{6,g} \tag{53}$$

$$WOPO_{4,s} + 3/7\,WP_s + 10/7\,I_{2,g} \rightleftharpoons 10/7\,WO_2I_{2,g} + 5/14\,P_4O_{6,g} \tag{54}$$

$$WP_2O_{7,s} + 4/7\,WP_s + 11/7\,I_{2,g} \rightleftharpoons 11/7\,WO_2I_{2,g} + {}^{9}\!/_{14}\,P_4O_{6,g} \tag{55}$$

Model calculations on the chemical transport of $Mg_2P_2O_7$ and $Mn_2P_2O_7$ under the same conditions also support the idea of a decisive contribution of "reduced" phosphorus oxides, namely $P_4O_{6,g}$, to the transport of anhydrous phosphates with iodine under reducing conditions.[146] By taking $P_4O_{6,g}$ into consideration with $\Delta_B H_{298}(P_4O_{6,g}) = -440\ \text{kcal mol}^{-1}$, a value that is used as a fit parameter, it is possible to describe the experiment quantitatively. Both the dependence of the transport rates of $Mg_2P_2O_7$ and $Mn_2P_2O_7$ on the mean temperature and their dependence on the amount of transport agent can be calculated reliably.

6.4. Transition Metal Niobates

The transport behavior of niobates differ in various thermochemical aspects from that of the anhydrous sulfates and phosphates, both of which contain a volatile oxide component (acid anhydride). In contrast, transport of niobates can only take place when both Nb_2O_5 and its bonding partner react with the respective transport agent to form volatile compounds. The heat of neutralization of the formal reaction of formation between the basic (MO, M_2O_3) and the acidic oxides (Nb_2O_5, SO_3, P_4O_{10}) is much lower (10–20 kcal per mol Nb_2O_5 with the formation of MNb_2O_6) for niobates[159] than for sulfates and phosphates. It follows that the activities of the binary components of the niobates do not differ much from those of the pure oxides. The equilibrium partial pressures in the transport of niobates resemble those observed in the transport of the binary components under similar conditions.[150, 151, 159] Clear differences are seen however, as expected, in the transport of niobates with a very high content of Nb_2O_5 or the second component.

The determining equilibria for the transport of $NiNb_2O_6$ or $ScNbO_4$ with chlorine or $NbCl_5$ appear to be representative for many other niobates [Eq. (56)–(58)].

$$NiNb_2O_{6,s} + 4\,Cl_{2,g} \rightleftharpoons NiCl_{2,g} + 2\,NbOCl_{3,g} + 2\,O_{2,g} \quad (56)$$

$$ScNbO_{4,s} + 3\,Cl_{2,g} \rightleftharpoons ScCl_{3,g} + NbOCl_{3,g} + 3/2\,O_{2,g} \quad (57)$$

$$ScNbO_{4,s} + 3\,NbCl_{5,g} \rightleftharpoons ScCl_{3,g} + 4\,NbOCl_{3,g} \quad (58)$$

Initial experiments and thermodynamic analyses of the transport of niobates and several other ternary oxides have been performed by Emmenegger.[150, 151] Very extensive experimental investigations (Table 6) and a critical comparison of the detailed thermodynamic model calculations were performed for the systems M/Nb/O (M = Sc, [152] Hf, Zr,[111] V, Cr, Mn,[153] Fe, Co,[154] Ni,[155] Cu,[156, 157] Zn, Cd[158]) at a later date.[159] A very unfavorable influence on the transport of niobates was shown for the unavoidable traces of moisture (ca. 10^{-5} mol H_2O per ampoule),[113] which are desorbed from the wall of the silica ampoule. Thermodynamic modeling shows that this behavior is caused on one hand by an increase in the total pressure. However, the release of oxygen is more important as shown in Equation (59), whereby the heterogeneous equilibria such as in Equation (57) and (58) are shifted to the reactant side.

$$2\,H_2O_g + 2\,Cl_{2,g} \rightleftharpoons 4\,HCl_g + O_{2,g} \quad (59)$$

These effects are certainly significant for all transport experiments with oxides and chlorine as the TA.

The delimitation of the enthalpy of formation for niobates MNb_2O_6 (M = Mn, Fe, Co, Ni, Cu, Zn, Cd) by means of the observations (composition of deposits, transport rates) for the transport experiments is also worth mention.[159]

7. Ternary Oxides of the Rare Earths, Thorium, and Uranium

Crystals of chalcogenides, in particular the binary and ternary oxides of the rare earths, can only be grown with great effort from melts because of their high melting points.[160] In addition, complete reaction to a ternary compound can only be achieved at relatively high temperatures (e.g. > 1400 °C) if one of the components is high melting. If crystallization by sublimation is at all possible, it will also require very high temperatures. Phases that are metastable or stable only at fairly low temperatures are hardly accessible in this way. This also applies to compounds such as the multicomponent oxychlorides of the rare earths (Section 8), that are thermally labile and cannot be melted without decomposition. In such cases, preparative chemical transport experiments would be advantageous (Table 7).

For extremely stable oxides such as La_2O_3, chlorine appeared to be promising as a transport agent. However, as a result of the above-mentioned formation of $LaOCl_s$, [Eq. (29)] in our experiment in a silica ampoule,[161] the yellow color of the added gaseous chloride ($p(Cl_2) = 1$ atm at RT) disappeared completely and a transport reaction with the formation of $LaCl_{3,g}$ and oxygen did not take place. All other Ln_2O_3 compounds apparently react like La_2O_3, since the oxide of the heaviest rare-earth metal, Lu_2O_3, showed the same behavior in the presence of chlorine (1050 → 950 °C).[162]

Ternary compounds react in a similar fashion if they are rich in Ln_2O_3. The niobate and tantalate, La_3NbO_7 and La_3TaO_7, for example, are also decomposed by chlorine to form

Table 6. Transition metal niobates. In all cases chemical transport occurs as a result of endothermic reaction with the respective transport medium.

Niobate	Temperatures [°C]	Transport agent	$\dot{m}$ [mg h^{-1}]	Comments	Ref.
$Sc_{11}Nb_3O_{24}$	1100 → 1000	Cl_2		also $ScNbO_4$ and "$Sc_{1/3}NbO_3$"[a] at T_1	[159]
$ScNbO_4$	1100 → 1000	a) Cl_2	ca. 0.02		[152]
		b) $Cl_2/NbCl_5$	≤ 0.6		[152]
$TiNb_{14}O_{37}$	850 → 750	Cl_2 (1 atm at RT)		addition of $NbCl_5$ and $TiCl_4$	[267]
$VNbO_4$	1020 → 880	a) NH_4Cl	ca. 0.1		
		b) Cl_2		partial oxidation with formation of $(V, Nb)_{12}O_{29}$ at T_1 and $(V, Nb)O_2$ at T_2	[159]
$CrNbO_4$	1020 → 960	Cl_2	≤ 1	lower temps (840 → 780) lead to light-green $CrNb_{11}O_{29}$ at T_1[b]	[159]
$MnNb_2O_4$	1020 → 960	Cl_2	≤ 6		[150, 159]
$FeNb_2O_4$	1020 → 960	a) NH_4Cl	≤ 1	larger amounts of TA at T_2 lead to the formation of $(Fe, Nb)_{11}O_{29}$	[150, 159]
		b) Cl_2		complete oxidation with the formation of $FeNbO_4$ and $FeNb_{11}O_{29}$	[150, 159]
$FeNbO_4$	1000 → 900	Cl_2		$FeNbO_4$ (wolframite type); 860 → 640 leads to metastable $FeNbO_4$ as the $GaNbO_4$ type	[268]
$CoNb_2O_4$	1020 → 960	a) Cl_2	≤ 5	larger amounts of TA lead to the formation of $(Co, Nb)_{11}O_{29}$ and/or H-Nb_2O_5	[150, 159, 154]
		b) NH_4X (X = Cl, Br, I)	≤ 2	$(Co, Nb)_{12}O_{29}$ at larger TA amounts	[150, 159, 154]
$NiNb_2O_4$	1020 → 960	a) Cl_2	≤ 5	formation of $(Ni, Nb)_{11}O_{29}$ and/or H-Nb_2O_5	[150, 159, 155]
		b) NH_4Cl	≤ 0.4	Ni at T_1	[150, 159, 155]

[a] The phase shows a primitive cubic Guinier diagram; no other characterization was given. [b] The formation of the phase is only possible in a temperature gradient, it is possible that it is metastable towards decomposition to Nb_2O_5 and $CrNbO_4$.

Table 7. Rare-earth niobates and tantalates a) crystallized for the first time by endothermic chemical transport reactions with chlorine ($p(Cl_2) = 1$ atm at RT) and b) formed the first time by deposition from the gas phase and only obtainable by this method (probably metastable).

Compound	Temperature [°C]	Explanations	Ref.
$LaNbO_4$	1090/1000[a]	mostly deposits with Nb-rich phases (a)	[161, 269]
$CeNbO_4$	1000/900	forms alongside Nb-rich phases at $p(Cl_2, RT) = 0.5$ atm (a)	[203]
$La_{1/3}NbO_3$	1100/1000[b]	defect perowskite (a)	[161]
$LaNb_3O_9$	1100/1000[b]	monoclinic modification (b) transforms irreversibly at 1300 °C to $La_{1/3}NbO_3$	[161, 166]
$Ce_{1/3}NbO_3$	1100/1000[b]	exp. with $p(Cl_2, RT) \approx 0.5$ atm or with 5 mg NH_4Cl; defect perowskite (a)	[203]
$CeNb_3O_9$	950/900	exp. with 5 mg NH_4Cl; monoclinic like $LaNb_3O_9$ (b)	[203, 166]
$PrNb_3O_9$	950/900	monoclinic crystals (a) only at $T_2 = 950\,°C$! Exp. with 5 mg NH_4Cl	[270, 203, 271]
$LaNb_5O_{14}$	1050/950[b]	(a)	[161, 203, 167]
$CeNb_5O_{14}$	1100/1000[b]	(a)	[203]
$LaNb_7O_{19}$	900/800[c]	(b), at 1000 °C irreversible separation into $LaNb_5O_{14}$ and Nb_2O_5	[203, 272, 182]
$CeNb_7O_{19}$	850/800	(b), thermal characteristics similar to $LaNb_7O_{19}$	[203]
$PrNb_7O_{19}$	800/750	(b), like $LaNb_7O_{19}$	[203]
$NdNb_7O_{19}$	800/750	(b) heterogeneous transport product, otherwise like $LaNb_7O_{19}$	[203]
$LaTaO_4$	1050/950[d]	(a)	[161, 273]
$CeTaO_4$	(1100/1000)	(a), exothermic react.: 1000 → 1100 °C only with a reducing gas phase $CO + Br_2$ from $CO_2 + CBr_4$	[109]
$PrTaO_4$	1120/1020	(a)	[209]
$NdTaO_4$	1100/1000[e]	(a)	[109]
	980/880[f]	(a)	[109]
$La_{1/3}TaO_3$	1090/1000	(a), defect perowskite; single-phase SS is recommended	[161, 108]
$LaTa_3O_9$	1090/1000	(b), lower $p(Cl_2)$ as with $La_{1/3}TaO_3$, "bronze-type" structure, transforms irreversibly at 1100 °C to $La_{1/3}TaO_3$	[161, 108, 164]
$Ce_{1/3}TaO_3$	1100/1000	(a), defect perowskite	[109]
$CeTa_3O_9$	1090/1000[g]	(b), orthorhombic "bronze-type" structure as with La, alongside $Ce_{1/3}TaO_3$, also monoclinic, bronze-type structure, above 1200 °C both transform irreversibly to $Ce_{1/3}TaO_3$	[109, 274]
$Pr_{1/3}TaO_3$	1100/1000	(a), orthorhombic defect perowskite	[209]
$PrTa_3O_9$	1100/1020[h]	(b), difficult to reproduce; monoclinic structure closely related to $LaNb_3O_9$[i]	[275, 276]
$Nd_{1/3}TaO_3$	1100/1000	(a), orthorhombic defect perowskite only in the SS!	[109]
$NdTa_3O_9$	1100/1000[h,j]	(b), Structure like $PrTa_3O_9$[i], transforms irreversibly at 1200 °C to $Pr_{1/3}TaO_3$	[109, 275]
"$LaTa_5O_{14}$"	1390/1300	(a), forms above $T \gg 1100\,°C$, corresponds to $La_{4.67}Ta_{22}O_{62}$	[108, 109, 277]
$LaTa_7O_{19}$	1120/1050[k]	(a), decomposition to $LaTa_5O_{14} + Ta_2O_5$ at 1500 °C	[273, 165]
$CeTa_7O_{19}$	1100/1000[l]	(a)	[108, 163]
$PrTa_7O_{19}$	1120/1020	(a), lower $p(Cl_2)$ recommended	[209]
$NdTa_7O_{19}$	1100/1000[l]	(a)	[108, 163]

[a] $LaNbO_4$ can also be transported well with HBr (addition of 50 mg NH_4Br).[269] [b] The appearance of additional, partially Nb-rich phases ($LaNb_5O_{14}$; H-Nb_2O_5) can be suppressed by a slight temperature gradient.[269] [c] Instead of Cl_2, the addition of an oxychloride such as LaOCl or $La_2NbO_4Cl_3$ is advantageous. Powder can also be obtained by isothermal heating with Cl_2. [d] Ta_2O_5-rich phases also occur (e.g. $La_{1/3}TaO_3$).[108] [e] Starting solid: monoclinic $NdTaO_4$. [f] Starting solid: mixture Nd_2O_3:Ta_2O_5 1:1. [g] SS = CeO_2:Ta_2O_5:Ta 5:7:1. [h] Tribochemical transformation into a modification with higher density that is also monoclinic.[278] [i] Mainly $Ln_{1/3}TaO_3$ precipitates. [j] Starting solid = mixture Nd_2O_3:Ta_2O_5 1:3. [k] Ta_2O_5-poor phases also occur ($La_{1/3}TaO_3$, $LaTa_3O_9$).[273] [l] Higher proportion of $LnTa_7O_{19}$ with the addition of some (8 mg) V (VCl_4, $VOCl_3$).

oxychlorides and oxide phases of lower La content.[109, 161] The titanate Ln_2TiO_5 decompose in transport experiments with Cl_2 to form LnOCl and $Ln_2Ti_2O_7$ (Ln = La, Pr, Nd, Sm, Eu, Gd) according to Equation (61).[162]

Ternary oxides of low activity do not react fully to LnOCl [Eq. (29)] when chlorine is present; endothermic equilibria such as those formed with the *rare-earth niobates and tantalates*[163] become established [Eq. (60)], which allow chemical transport to occur (see also $NdNbO_4$ (Figure 5j).[270])

$$LaNbO_{4,s} + 3\,Cl_{2,g} \rightleftharpoons LaCl_{3,g} + NbOCl_{3,g} + 3/2\,O_{2,g} \qquad (60)$$

Therefore in the system La_2O_3/Ta_2O_5, with the exception of $LaTaO_4$ and $La_{1/3}TaO_3$, the new, probably metastable phase $LaTa_3O_9$[164] and the non-congruent melting $LaTa_7O_{19}$[165] could be crystallized for the first time. The phases $LaNb_3O_9$[166] and $LaNb_7O_{19}$[167] which occur in the La_2O_3/Nb_2O_5 system could only be obtained by means of chemical transport and are considered to be metastable.

Of the few rare-earth oxo compounds that were crystallized by chemical transport before the ternary oxides listed in Table 6, $LaPO_4$ deserves a special mention (Section 6.3).[168] Early efforts to grow crystals of $Y_3Fe_5O_{12}$ and $Gd_3Fe_5O_{12}$, in particular, in which HCl, CCl_4, and $Cl_2 + TeCl_4$ were used as transport agents,[169, 170] were carried out with a view to the potential physical applications of garnets.

Many of the compounds that can be transported in temperature gradients (Table 6) can also be produced and crystallized by the so-called "short-path transport" method (see Section 2.3); the temperatures used are similar to those of the experiments in a temperature gradient. If compounds cannot be obtained in this way by the action of a mineralizer but only by deposition in a temperature gradient, that means through a sufficiently supersaturated gas phase, they are considered to be "metastable".

The phase distribution in the Ln_2O_3/TiO_2 system is already widely understood.[171] Chemical transport experiments, however, had not been performed until the investigations by Hübner.[162] With Cl_2 as the transport agent, the undesirable side reaction to yield LnOCl [Eq. (29) and Eq. (61)] could be suppressed only for titanates with a ratio of $Ln/Ti \leq 1$.

$$2\,Ln_2TiO_{5,s} + Cl_{2,g} \rightleftharpoons 2\,LnOCl_s + Ln_2Ti_2O_{7,s} + 1/2\,O_{2,g} \quad (61)$$
$$(Ln = La, Pr, Nd, Sm, Eu, Gd)$$

All titanates $Ln_2Ti_2O_7$ from Ln = Nd (Ln = Nd, Sm (Figure 5g), Eu–Lu)[162] migrate in temperature gradients (1050 → 950°). Sometimes a small amount of rutile (TiO_2) was deposited as well, probably as a result of reactions with the wall (silica ampoule) which consume Ln_2O_3. Chlorine proved to be effective as a TA[162] and also in some cases, $HgCl_2$.[172] The compound $Ce_2Ti_2O_7$, which is sensitive to oxidation, could not be transported with Cl_2 or with HCl,[171] but transport did succeed with the addition of NH_4Cl or $HgCl_2$ (1050 → 950 °C).[173]

The crystallization of monoclinic $Nd_2Ti_4O_{11}$ in a short-path transport experiment[174] is worth mentioning as is that of $Nd_4Ti_9O_{24}$ (Figure 5o), which could be transported in a temperature gradient (1000 → 900 °C) with chlorine.[175] Recently the short-path transport of $Pr_4Ti_9O_{24}$ succeeded,[172] whereas transport reactions with the compounds $La_4Ti_9O_{24}$ and $Ce_4Ti_9O_{24}$, which are also isotypic to $Nd_4Ti_9O_{24}$, could not be realized.[162]

The new silicate-titanate $Ce_2Ti_2SiO_9$ was produced in the sink (1050 → 900 °C) when the binary oxides were used as the reactants and SiO_2 was present in excess with NH_4Cl.[176]

ThO_2 migrates with the addition of Cl_2 or NH_4Cl only with extremely low transport rates. As in the case of La_2O_3, an unwanted side reaction is the problem, which in this case occurs with the wall of the silica ampoule and leads to the formation of thermodynamically stable $ThSiO_4$ (α- or at least the β-form). $ThSiO_4$ also migrates together with small amounts of ThO_2 to the cooler zone (e.g. 1050 → 950 °C).[177] We are not aware at present of an effective method of chemically transporting ThO_2.

The unwanted effect of the formation of $ThSiO_4$ can be essentially suppressed in transport experiments with *thorium niobates*, or *tantalates* apparently because of the stability of such compounds. With the help of Cl_2 or NH_4Cl as the TA, it was possible[177, 178] to deposit the following ternary well-crystallized phases in the cooler zone: $Th_2Nb_2O_9$,[177] $Th_2Ta_2O_9$,[179] $ThNb_2O_7$,[180] $ThTa_2O_7$,[181] $Th_2Ta_6O_{19}$,[182] $ThNb_4O_{12}$, $ThTa_4O_{12}$,[177] $Th_4Ta_{18}O_{53}$ (TA: $Cl_2 + TaCl_5$),[183] and also α-$ThTi_2O_6$ (TA: $Cl_2 + S$).[184]

Up to now $ThNb_2O_7$, $ThTa_2O_7$, and $Th_2Ta_6O_{19}$ could only be obtained by chemical transport or with the help of the mineralizing effect of Cl_2, since they may be metastable.

A range of transport agents are applicable for UO_2. In particular $TeCl_4$[102, 185] and Cl_2,[186, 187] but also Br_2, $Br_2 + S$, I_2, and HCl have proven useful.[187]

Mixed crystals $U_{1-x}Th_xO_2$ were deposited with the help of the transport agent HCl.[188] Transport experiments with the addition of HCl or $Br_2 + S$ were successful for U_3O_8.[188] It was possible to transport U_4O_9 with Cl_2, Br_2, or I_2.[189]

In addition, the ternary compounds UNb_6O_{16} (TA NH_4Cl),[190] γ-$UNbO_5$[191] and UNb_2O_7 (TA $Cl_2 + NbCl_5$),[192] $U_4Ta_{18}O_{53}$ (TA $Cl_2 + TaCl_5$)[183] and $U_2Ta_6O_{19}$ (TA HCl)[193] could be crystallized by means of CT. According to the literature,[189] there is evidence that $UOCl_{2,g}$ or $UO_2Cl_{2,g}$ participates in the transport process. For the CT of $UTaO_5$, a reaction according to Equation (62) was supported by mass spectrometry experiments.[193, 194]

$$UTaO_{5,s} + 5/2\,Cl_{2,g} \rightleftharpoons UO_2Cl_{2,g} + TaOCl_{3,g} + O_{2,g} \quad (62)$$

8. Polynary Oxychlorides of the Rare Earths

It proved to be extremely productive to undertake an extensive study of the "failure" of Ln_2O_3 to form in the presence of the transport agent chlorine with the formation of LnOCl [Eq. (29)] from ternary and multicomponent compounds.[109] Ternary oxides can, as the example of Ln_2TiO_5 [Eq. (61)] has already shown, also react with Cl_2 to form LnOCl. But here new, polynary oxychlorides are produced: Starting from Pr_2TiO_5, a transport experiment with Cl_2 [$p(Cl_2; RT) = 1$ atm; 1050 → 900 °C] results in the deposition of $Pr_2Ti_3O_8Cl_2$ alongside PrOCl in the cooler zone. [162, 195] We also observed similar behavior with Ln_3TaO_7 and Ln_3NbO_7. The reactions, in which Cl_2 was obviously consumed, proceeded in a more complicated fashion, however, since traces of moisture were also involved (wall of the silica tubes) [Eq. (63)].

$$\begin{aligned}&3\,La_3TaO_{7,s} + 6\,Cl_{2,s} + H_2O_g \rightarrow \\ &\qquad 3\,La_3TaO_5(OH)Cl_{3,s} + LaTaO_{4,s} + 2\,LaCl_{3,s} + 3\,O_{2,g}\end{aligned} \quad (63)$$

When the reaction products are heated (1400 °C) in air Equation (63) quantitatively reversed. If H_2O is present in stoichiometric amounts, pure $La_3TaO_5(OH)Cl_3$ is formed in a Cl_2 atmosphere according to Equation (64),[196, 197] and can be transported in a temperature gradient of 1080 → 980 °C.

$$6\,LaOCl_s + Ta_2O_{5,s} + H_2O_g \rightarrow 2\,La_3TaO_5(OH)Cl_{3,s} \quad (64)$$

In a principally similar fashion, new compounds in the Ln/Ti/O/Cl, Ln/V/O/Cl, Ln/Nb/O/Cl, and Ln/Ta/O/Cl systems could be identified by deposition and crystallization in temperature gradients followed by structural characterization ($La_3TiO_4Cl_5$,[198] $Ln_2Ti_3O_8Cl_2$ (Ln = Ce (Figure 5s),[172] Pr (Figure 5c), Nd),[195] $LnTiO_3Cl$ (Ln = Sm – Lu),[199, 200] $Ln_3VO_4Cl_6$ (La – Nd),[201] $Ln_{12.33}V_6O_{23}(OH)Cl_{20}$ (Ln = La, Ce),[202] $Ln_3NbO_4Cl_6$ (Ln = La,[163] Ce,[203] Pr,[204, 205] Nd [204]), $Ln_3TaO_4Cl_6$ (La – Nd),[109, 206] $La_2NbO_4Cl_3$,[203] $Ln_2TaO_4Cl_3$ (Ln = La, Ce),[207] $Ln_3NbO_5(OH)Cl_3$ (Ln = La, Pr, Nd),[204] $Ln_3TaO_5(OH)Cl_3$ (Ln = La, Pr, Nd),[197, 208, 209] $Ln_2M^{4+}NbO_6Cl_3$ (Ln = La, Pr, Nd; M^{4+} = Ce, U; Ln = La, Pr, Nd, Sm – Dy; M^{4+} = Th),[204, 210] $Ln_2M^{4+}TaO_6Cl_3$ (Ln = La – Nd, M^{4+} = Ce, U; Ln = La – Ho, M^{4+} = Th),[208, 210, 211] (Ln, Ce)$_{3.25}MO_6Cl_{3.5-x}$

(Ln = La, Ce, Pr; M = Nb, Ta),[212] $(Ln, Ce)_{3.5}MO_6Cl_{4-x}$ (Ln = La, Pr, Nd, Sm; M = Nb, Ta),[212] $Ln_2Ta_2O_7Cl_2$ (Ln = Pr, Nd,[213] Sm[214]), $Nd_{7.33}Ta_8O_{28}Cl_6$[215]).

As is known from the given compositions, $Ln_2M^{4+}NbO_6Cl_3$ and $Ln_2M^{4+}TaO_6Cl_3$, including $M^{4+} = Th^{4+}$ and U^{4+}, can be synthesized and transported. This type of compound has the $La_3WO_6Cl_3$ structure type and also crystallizes (TA = Cl_2) with U^{6+} as $Ln_3UO_6Cl_3$ (Ln = La, Pr, Nd).[216]

It should be mentioned that it was not possible to synthesize isotypic compounds with other larger or smaller rare-earth ions in some of the compositions given here. Therefore it appeared reasonable that experiments with different rare earths have been carried out to establish the borders of the crystal-chemical "existence ranges".

9. Chemical Transport of Metal Halides

A large number of the binary metal–halogen compounds such as trihalides (AlX_3, X = Cl, Br, I; FeX_3, X = Cl, Br), tetrahalides (TiX_4, $SiCl_4$, SnX_4, X = Cl, Br, I), and pentahalides (VCl_5, $NbCl_5$, $TaCl_5$) already demonstrate considerable volatility at even slightly raised temperatures. In other cases it can be advantageous for preparative reasons to undertake measures to improve the volatility, for example with the less volatile compounds $CrCl_2$, $CrCl_3$, $LnCl_3$, and chlorides of the alkali and alkaline earth metals.

In individual cases, transport via a gaseous halide in a higher oxidation state was successful [Eq. (65) and (66)]. The compounds FeI_3[217]and $CrCl_4$ are, in fact, only known as gas molecules.

$$2\,FeX_{2,s} + X_{2,g} \rightleftharpoons Fe_2X_{6,g} \qquad (X \rightleftharpoons Cl, Br, I) \tag{65}$$

$$2\,CrCl_{3,s} + Cl_{2,g} \rightleftharpoons 2\,CrCl_{4,g} \tag{66}$$

Much more frequent are cases in which the greater volatility of a so-called "gas complex" is utilized, whereby mainly $AlCl_3$, $FeCl_3$, or $GaCl_3$ are used as complexing agents, as studied extensively by Schäfer.[218, 219]

The synthesis and separation of $CrCl_2$ (350 → 250 °C)[220] [Eq. (67)] and $CrCl_3$ (500 → 400 °C)[221] [Eq. (68)] were improved.

$$CrCl_{2,s} + 2\,AlCl_{3,g} \rightleftharpoons CrAl_2Cl_{8,g} \tag{67}$$

$$CrCl_{3,s} + 3\,AlCl_{3,g} \rightleftharpoons CrAl_3Cl_{12,g} \tag{68}$$

$CuCl_2$, which releases chlorine when heated, can also be transported in the form of the beautiful blue gas complex $CuAl_2Cl_8$.[222]

"Gas complexing agents" have also proven useful for the vaporization of rare-earth halides, as the extensive investigation of the phases Eu_5Cl_{11}, Eu_4Cl_9,and $Eu_{14}Cl_{33}$[223, 224] in the $EuCl_2/EuCl_3$ system has shown. It was possible to transport Eu_5Cl_{11} in the temperature gradient 480 → 545 °C and $EuCl_3$ at 480 → 380 °C.[225]

Trihalides cannot, however, be used for the formation of gas complexes, if oxides (O-containing solids) are to be transported, since the thermodynamic stability of the corresponding oxide, in particular Al_2O_3, would lead to the complete consumption of the trihalide. This reaction behavior can be utilized if the halogenation of rare-earth oxides and, at the same time, the separation of the resulting RE halide LnX_3 (Ln: La–Nd, Sm–Tb; X = Cl, Br) in the form of a suitable gas complex is attempted.[226, 227] The sesquioxides Ln_2O_3 react with AlX_3 in accordance with Equation (69). If higher rare-earth oxides (e.g. CeO_2, "Tb_4O_7") are used, additional chlorine is released [Eq. (70)].

$$2\,Ln_2O_{3,s} + 3\,Al_2X_{6,g} \rightleftharpoons 4\,LnX_{3,s} + 6\,AlOX_s \qquad (X = Cl, Br) \tag{69}$$

$$2\,CeO_{2,s} + 2\,Al_2Cl_{6,g} \rightleftharpoons 2\,CeCl_{3,s} + 4\,AlOCl_s + Cl_{2,g} \tag{70}$$

The separation of the RE halides is subsequently achieved by chemical transport with excess AlX_3. For the transport system $NdCl_3/Al_2Cl_6$, the gas complexes $NdAl_3Cl_{12}$ and $NdAl_4Cl_{15}$ have been detected [Eq. (71) and (72)].[228]

$$NdCl_{3,s} + 3/2\,Al_2Cl_{6,g} \rightleftharpoons NdAl_3Cl_{12,g} \tag{71}$$

$$NdCl_{3,s} + 2\,Al_2Cl_{6,g} \rightleftharpoons NdAl_4Cl_{15,g} \tag{72}$$

In many cases (e.g. MAl_2Cl_8, M = Cu,[229] Pd[230]; $LnAl_3Cl_{12}$, Ln = Tb, Dy, Ho;[231] $LnAl_3Br_{12}$, Ln = La–Nd, Sm, Gd[227], it was possible to isolate and crystallize the gas complexes.

Since the volatility of *metal fluorides* is much lower, a suitable transport reaction is of particular interest. The use of silicon halides (Cl, Br, I) as TA enables the utilization of the thermodynamic stability and, at the same time, high volatility of SiF_4 (GeF_4) [Eq. (73)].[232] Experiments with MgF_2 pointed to a similar transport reaction [Eq. (74)].[172]

$$4\,ScF_{3,s} + 3\,SiCl_{4,g} \rightleftharpoons 4\,ScCl_{3,g} + 3\,SiF_{4,g} \tag{73}$$

$$2\,MgF_{2,s} + SiI_{4,g} \rightleftharpoons 2\,MgI_{2,g} + SiF_{4,g} \tag{74}$$

It is not yet clear why $MgF_{2,s}$ migrates in a temperature gradient (1000 → 900 °C) even when mere iodine is added. A reaction in which $MgI_{2,g}$ and $F_{2,g}$ are formed should be excluded with certainty due to the low oxidation capability of iodine.[172]

10. Summary and Outlook

The broad new fields of application which have been opened up by the transport methods in the past 15 years leave no room for doubt that also in the future, chemical transport reactions will continue to show great potential. Already in this attempt to describe the current situation we have failed, for obvious reasons, to discuss a series of interesting developments from our colleagues and from our own research group. Interesting information on the interpretation of the reaction processes could be obtained from investigations into the crystallization of compounds such as $Se_{17}(WCl_6)_2$ or $Te_6(WOCl_4)_2$ by the research group of J. Beck.[233, 234]Also the results of chemical transport experiments in non-isothermal plasmas by Veprek show promise for further potential applications in preparative solid-state chemistry.[235, 236, 237]

Some research which was not discussed here and which is partly still in progress concerns the chemical transport of germanates,[238, 239] silicates (e.g. Ni_2SiO_4[240] or $Yb_2Si_2O_7$,[172] see Figure 5 a)and silicate halides such as $Ln_3SiO_4Cl_5$,[241] $Ln_3Si_2O_8Cl$,[172] or $Mn_3SiO_4F_2$.[242] Further new substance classes will be investigated in the coming years, so that the broad applicability of the method to the synthesis, purification, and crystallization of solids will be of great use.

Finally we have also not discussed the many structural investigations of single crystals that were only accessible by the described transport experiments. Information on this important aspect of the research field can be obtained from the cited literature. The potential of the transport method for the synthesis of crystals for physical studies will continue to be considerable. In order to obtain the "large" crystals that are frequently necessary, it is possible that some of the already available procedures could help to prevent the growth defects, additional nuclei formation etc., by means of the "gradient reversal" method described by Scholz,[243] or by the in situ observation (and control) of crystal growth.[244, 245]

With our review we would also like to encourage the greater use of chemical transport as an investigative method for the study of equilibrium gas phases and for the development of new methods for the clarification of previously not understood transport processes. In particular, this includes the qualitative and quantitative detection of previously unknown gas molecules, but also the less spectacular thermodynamic characterization of participating solids and gas molecules.

The time dependence of the deposition of compounds with homogeneity ranges (mixed crystals, nonstoichiometric compounds) and their thermochemical description (prediction) should also receive greater attention in the future. Important results in this area have already been provided by Oppermann and Krabbes, and Binnewies. We believe that with suitable transport experiments, information on the thermodynamics of mixed phases can also be obtained. Technically interesting questions such as the directed adjustment of certain mixing or doping ratios make this field particularly interesting.

Up to now the description of the influence of convection on the TR has been difficult. In particular there is the question of how well the "simple" formulations describe the experimental characteristics.

It is certain that the possibility to synthesize and crystallize new classes of compounds through an in-depth understanding of the reactions between the solid and the gas phase will ensure the continuing fascination of the method in the future.

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