CHEMICAL TRANSPORT REACTIONS

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Introduction
and Historical Review

Chemical transport reactions are those in which a solid or liquid substance A reacts with a gas to form exclusively vapor phase reaction products, which, in turn, undergo the reverse reaction at a different place in the system, resulting in the reformation of A.

$$iA_{(s,l)} + kB_{(g)} + \cdots = jC_{(g)} + \cdots \tag{1}$$
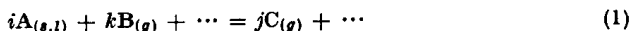
The process appears to be one of sublimation or distillation. Substance A, however, does not possess an appreciable vapor pressure at the applied temperatures. The substance is *transported chemically*. In addition to a reversible heterogeneous reaction, a concentration gradient must be established. The latter can be the result of temperature gradients, changes in the relative pressures, or the differences in the free energy of formation of two substances.

The transport of substances by means of heterogeneous reactions has been known for a long time.

Bunsen[1] mentioned, in connection with the hydrogen chloride content of volcanic gases, that Fe_2O_3 can migrate in a stream of HCl. The controlling feature in this case is the reversible nature of the reaction

$$Fe_2O_3 + 6\,HCl = 2\,FeCl_{3(g)} + 3\,H_2O_{(g)} \tag{2}$$
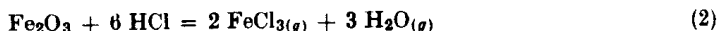
Similar reactions were utilized very successfully by the mineral chemists of the French School. Thus Sainte-Claire Deville[2] observed the corresponding transport of the oxides SnO_2, TiO_2, and MgO. He

reported on this as a part of his studies "on the artificial reproduction of crystalline minerals."

Troost and Hautefeuille transported silicon[3] and aluminum[4] in streams of the corresponding chlorides. These cases, as we know them today, are explained as the formation and disproportionation of the subchlorides,

$$Si_{(s)} + SiCl_{4(g)} = 2\ SiCl_{2(g)} \tag{3}$$

$$2\ Al_{(l)} + AlCl_{3(g)} = 3\ AlCl_{(g)} \tag{4}$$
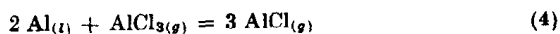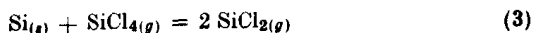
The first period of investigation extended from 1850 to 1890.

The second period began in 1925. Since then, van Arkel and de Boer[5,6] and later workers have developed processes for the purification of metals. These processes have become extremely well known and are of great practical value. The metal is vaporized as the iodide, which then decomposes on a hot filament.

$$Me_{(s)} + 0.5\ n\ I_{2(g)} = MeI_{n(g)} \tag{5}$$

$$Me_{(s)} + n\ I_{(g)} = MeI_{n(g)} \tag{6}$$
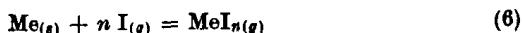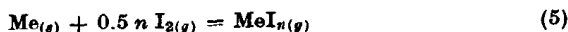
The thorough study by Biltz, Fischer, and Juza[7] "on the pneumatolytic transport of gold through chlorine" deserves special consideration. We shall discuss this point later.

For the naming of the class of reactions under consideration there are several precedents. One could go along with Biltz, Fischer, and Juza, and speak of "pneumatolytic transport." When, however, the expression "pneumatolysis" is used in the mineralogical sense, only part of the reactions that we consider here can be covered. "Catalytic distillation" or "subhalide distillation", a notation formulated by Gross[8] for reactions such as Eq. (4), is too narrow for the totality of the field. Troost and Hautefeuille described the migration of silicon in the presence of silicon tetrachloride as a "transport." Sainte-Claire Deville also used the latter term. We will use "chemical transport reactions."

This review indicates that the phemonena under consideration are not new by any means. Nevertheless, a third period of investigation started about 1950, and the field is an active one today.[9–15a] The following points make it clear that much profitable work remains to be done in the field:

Chemical transport reactions can, as will become clear later in this work, be applied in a considerably more versatile manner than has

been done so far. It is important not only to elucidate the principles more clearly, but also to exploit the reactions more fully.

One can predict the transport properties of a heterogeneous re-action simply and to a good approximation.

In place of the present qualitative observations, experiments can be carried out which will yield quantitative interpretations.

The systematic collection of observations of and references to transport reactions has brought to light a voluminous amount of prior knowledge. The latter will be treated in large part, but not exhaustively. Above all, characteristic and practically important examples, or examples which are interesting for other reasons, will be selected. In addition, use will be made of numerous, as yet un-published, observations from my own work.

Experimental and Theoretical Principles

Before the treatment of special reactions, general aspects which are valid in experimental and theoretical considerations will be discussed. In doing so the general equation will again be taken as the basis:

$$iA_{(s,l)} + kB_{(g)} = jC_{(g)}$$

It is useful to adopt the following conventions:

Equations are always written so that the *solid substance* to be transported appears on the left side. Such a convention is essential for later thermodynamic considerations.

Of the temperature symbols T_1 and T_2, the latter always indicates the higher temperature.

An arrow indicates the direction of the transport of the solid substance in the temperature gradient. The convention of writing $T_1 \rightarrow T_2$ also indicates the transport to a hotter zone.

2.1 Experimental Techniques

The transport of solid substances presupposes a motion of gas. One can distinguish processes which make use of gas stream diffusion or of thermal convection. When the reverse reaction proceeds rather extensively and rapidly with deposit of solid substance,* one makes use of open tubes and extremely simple flow techniques. In

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* Compare with the silicon transport in Section 3.1.2.2.

all other cases, closed diffusion and convection tubes are more advantageous.

One can choose procedures which are especially optional from the theoretical point of view (see Section 2.3). However, one often will discard these in favor of an easier preparation or higher transport yield, and then one will have to accept the resulting lower accuracy in the calculation of the transport yield.

2.1.1 FLOW METHODS

In the case that the transport medium B is already gaseous at room temperature and if the gas flows through a temperature gradient, then in principle the same arrangements can be used as for the equilibrium measurements with the flow methods. For this a space where the gas can stay for a fairly long time must be provided for the reverse reaction. As a rule, however, only a few arrangements are satisfactory. In the simplest case, the solid substance, A, is placed in a small vessel, which, in turn, is placed inside a tube of 10 mm diameter, for example. It is better, however, to have substance A in a granular form, packed loosely in the tube over a distance of a
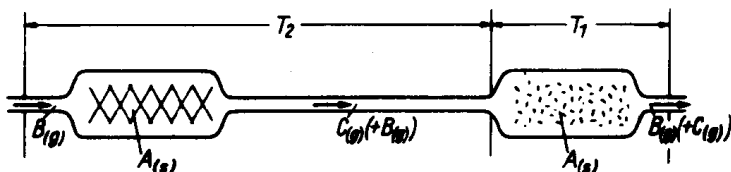
FIG. 1. Ideal flow arrangement for the transport of a solid substance in the temperature gradient; $iA_{(s)} + kB_{(g)} = jC_{(g)}$.

few centimeters. Gas B passes over the solid and, in the ideal case, equilibrates with it completely. At a different location in the tube at another temperature the reverse reaction takes place with the deposition of the solid substance A. For the afore-mentioned tube diameter and for temperatures of the solid above 500°C, gas flows of from 2 to 10 liters per hour (20°C, 1 atm) have usually proved to be satisfactory. When the reaction between the gas phase and the solid substance proceeds too slowly or when one is forced to use slow gas flow rates, larger amounts of solid and longer reaction zones are recommended; or one could make use of the arrangement as given on Fig. 1. It may also be profitable to recycle the gas.

Typical examples of the application of flow methods of this kind are the transport experiments with IrO_2 and RuO_2 in a stream of

oxygen (cf. Section 3.1.4.1.).

If the transport medium B has a sufficient saturation pressure only at elevated temperatures, then B is added to an inert carrier gas in a heated saturator, or B is (without carrier gas) vaporized at the beginning of the system. B then passes over solid A, transports it, and, at the end of the system, is condensed by cooling. In this procedure one can work with an open as well as a closed system. This technique has proved to be good, for example in the case of the Al transport (1000 → 650°C) in a stream of aluminum trichloride. The apparatus consisted of quartz with a liner of sintered corundum, in which part the transport reaction takes place.[16] The destruction of the wall of the quartz tube, owing to the reaction with the liquid aluminum was thus prevented.

Flow methods with a pressure gradient are also of interest. The equilibrium gas phase of a reaction, which proceeds with a decrease in the number of molecules, is lowered in total pressure by the outflow through a nozzle under isothermal conditions, so that the reverse reaction, i.e. the reformation of the solid reactant, occurs. The same effect is obtained by the addition of an inert gas. Figure 2 shows an arrangement suitable for this purpose which is based upon the carrier gas methods for equilibrium measurements.[17] Temperature and pressure gradients can be used simultaneously also.
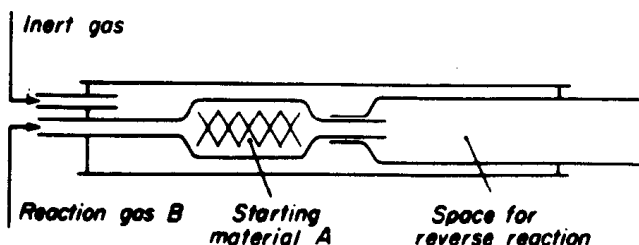
FIG. 2. Flow arrangement with the admixture of an inert gas.

2.1.2 GAS MOTION BY DIFFUSION

Diffusion methods are very widely used. Even simple glass or quartz tubes as pictured in Fig. 3a are suitable for many purposes. Systems with a more sharply defined diffusion space will be discussed in Section 2.3. The loading of the transport tube often can be done very simply, as for example, for preparative procedures. The solid material (or, as the case may be, the components from which the

final solid product is to be formed) is placed in a tube which is closed at one end; the transporting agent, e.g., I_2, Br_2, or NH_4Cl, is added, after which a constriction is made at an appropriate location on the tube, which is sealed off under vacuum, with the cooling of the start-ing material if necessary. The initial pressures of the transporting agent which are required at the transport temperature lie mostly between a few millimeters Hg and several atmospheres. The trans-porting agent iodine, suitable in many cases, is often used in amounts of 0.5 to 5 mg per centimeter^3 volume of the tube; at 1000°K this corresponds to an iodine pressure of from 0.16 to 1.6 atm.

If the transporting agent is a gas at room temperature (Cl_2, HCl, or O_2), as a rule it is possible simply to fill the tube at room tempera-ture with the transporting gas at atmospheric pressure.
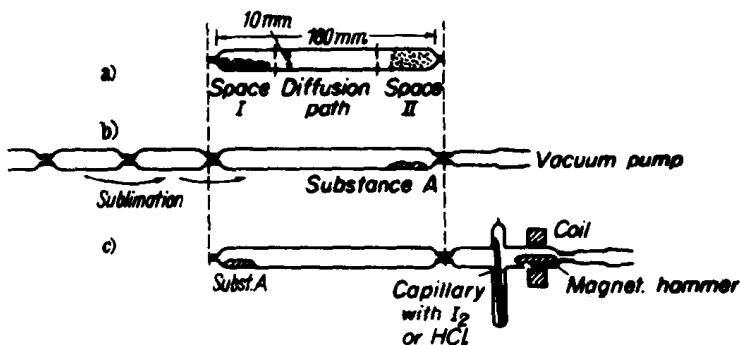
Fig. 3. The transport tube and its loading procedure (dimensions and substances serve as an example).

The situation is different when the transport experiments are designed to give quantitative data, i.e. when the object is to gain an insight into the transport mechanism. The loading of the transport tubes, in these cases, requires greater care, because even very small quantities of impurities can give rise to effects on the transport.[13,14] The tube, usually made of quartz glass, and the solid substance are degassed thoroughly in a high vacuum at a temperature of 1000°C, for example. Other substances are, if possible, sublimed several times in a high vacuum (Fig. 3b). Volatile substances like hydrogen chloride, chlorine, bromine, or iodine are condensed in separate runs into capillaries, which are then brought into the system. After the tube is sealed off from the pump, these capillary tubes are opened with

the magnetic breaker (Fig. 3c). If the transport tube is made of quartz and the iodine- or bromide-containing capillary of glass which has a low softening point, then the capillary can also be "blown out" by heating with a sharp torch.[11] This method has proved to be good. In each case, the content of the capillary is condensed near the solid substance. After the tube which contains the broken capillary has been sealed off, the transport tube will then look like one represented on Fig. 3a. It can now be heated in a temperature gradient.

In addition to these procedures, others, especially for the loading of transport tubes with gases, are described.[9,11,13,14,18] It is obvious that there are many variations for this loading of the tubes; compare, for example.[19]

If a certain amount of Cl_2 is to be introduced, K_2PbCl_6 can be decomposed at $\sim 250°C$. By heating a mixture of $AgI + V_2O_5$, I_2 can be liberated, and thus introduced into the transport tube.[19a] The same is also possible by means of a reaction between a mixture of AgI and $Ag_2Cr_2O_7$[19b] with molten $KHSO_4$. Procedures of this kind are especially useful in processes involving I^{131}.

The ability of quartz to reversibly absorb considerable quantities of water at higher temperatures,[20,20a] can give rise to disturbances or wrong conclusions.[14] When it is necessary to exclude hydrogen or its compounds completely, then it is possible to use quartz which has been melted electrically and which is consequently free of OH groups[14] (infrared spectra show no OH bands at 2.7 microns). In this case, the tube is not sealed off with a hydrogen–oxygen torch, but rather with a carbon electric torch.

Occasionally it is necessary to protect the quartz against attack by installing large, cylindrically shaped, sintered alumina cups which can be closed. Arrangements are made such that the transport reaction takes place in the alumina cup, while in the outside space, next to the quartz, no corrosive gas is present. In the temperature region where quartz softens, one can still work when one supports the walls of the quartz tube with a shield of *Pythagoras-Masse*. At even higher temperatures, in addition to special ceramic materials, metals like molybdenum, tungsten, and platinum are used as material for containers. Metal films can be converted to vials by rolling them over glass rods and pinching the ends together. Such a reaction vessel can be heated by direct passage of electric current.

It is not completely closed off from its surroundings and it can be evacuated and filled with gases. The pressures inside and outside are

equal and the loss of gaseous substances by diffusion is negligibly small. A solid that is placed in the vial can thus be transported along the heated zone in the natural temperature gradient.[21] Cater, Plante, and Gilles have described transport experiments in closed molybdenum containers.[22] At temperatures above 1300°C often hot wire systems are used.

If metals are transported onto a hot wire, as it happens in the iodine method of van Arkel and de Boer, then the gas motion takes place primarily by diffusion. The thermal convection is still insignificant at the low pressures that prevail as a rule. Figure 4 shows a hot wire system[23] which is extremely suitable for laboratory work; also compare.[24] Other apparatus used in the metal transport onto
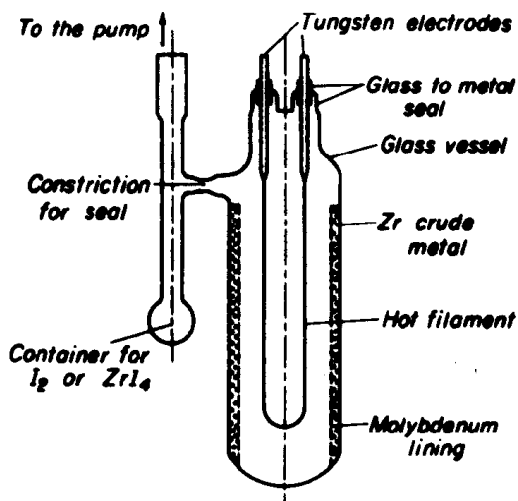
FIG. 4. Laboratory arrangement for the zirconium transport
by the iodide method according to Shapiro.[23]

a hot wire, suitable for use on a laboratory as well as a technical scale, have been reported by Shapiro.[23] The uranium transport, where molten uranium separates out on a hot wire, deserves special attention. The liquid metal drops into a receiver.[25] In this manner the transport can proceed uninterrupted.

In the case of metals like chromium, niobium, and tantalum, whose iodides are decomposed at relatively low temperatures, the hot wire can be replaced[26-27a] by a quartz or vycor vial which is heated internally, and which can be removed without disturbing the rest of the system.

2.1.3 Gas Motion by Thermal Convection

If, in addition to diffusion, convection occurs in the tube, then the transport yield can be increased considerably. This, for example, is observed when tubes with a diameter larger than 20 mm are placed in a sloping position in a temperature gradient with the hot part downwards, while the pressure inside the tube is several atmospheres (Fig. 5). In order to fill the tube, procedures such as those described
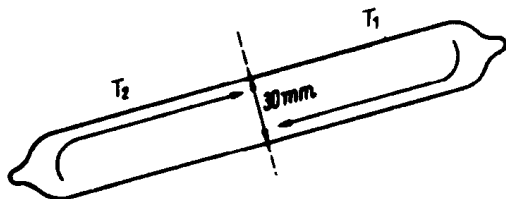

Fig. 5. Gas motion by thermal convection.
$T_2 > T_1$.

in Section 2.1.2 are at one's disposal. The procedure has proved to be good in the case of the transport of large quantities of silicon via its dihalides.[11] Figure 6 shows an arrangement which has also been used for the transport of silicon.[18] Because in this case SiF_4 is used as the transporting gas, the gas path can lie partly outside the furnace.

For a further discussion of convection, see Section 2.3.3.

2.1.4 Annealing and Temperature Gradients

This section will give some details concerning procedures used in our laboratories.

Temperature gradients T_2 with not greater than 500°C are produced by placing two electrically heated, unalloyed aluminum blocks next to each other. Each aluminum block is 300 mm long, with an outside diameter of 80 mm and an inside diameter of 30 mm. Each is provided on the outside with a groove in which the heating coil is placed. The latter is insulated by porcelain beads held in place by a covering of asbestos tape or paper. Contact thermometers are used to regulate the temperature.

At higher temperatures ordinary tube furnaces or *Silit* tube furnaces are used, in which it is possible to make use of the natural temperature gradient. It is better to use two good heat-conducting, temperature-equalizing bodies (silver, nonscaling steel). More often

than not, however, one prefers to use tube furnaces provided with two consecutive heating coils which can be regulated independently: "transport furnaces."

In growing larger single crystals, the transport tube has been pulled through the natural temperature gradient of an electric furnace. The speed with which the tube was pulled through amounted to 0.01 to 1 cm per hour, for instance. The temperature gradient in the tube is reversed during this particular heating process. This resulted in the removal, by transport, of the nuclei which were initially at the locations where the crystallizing process last occurred. The deposition of polycrystalline materials can thus be prevented.

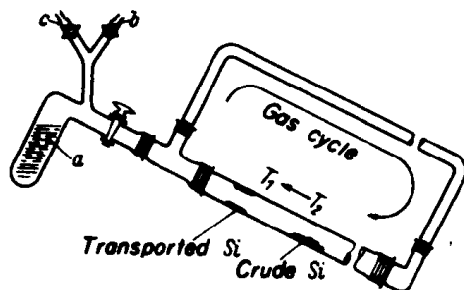The same result may be accomplished by keeping the tube at a

FIG. 6. Gas motion by thermal convection. Apparatus designed by Kempter and Alvarez-Tostado[18] for silicon transport in an atmosphere of SiF_4: (a) $BaSiF_6$, which yields SiF_4 on heating; (b) stopcock for the introduction of inert gas (He); (c) tube leading to the vacuum pump.

fixed location in the transport furnace, while the heating coils which make up the furnace and which are mutually independent are set for a temperature–time program.

Recently a furnace came into use in which temperature differences were not produced by local heating, but by intermittent heating. Suitable control devices keep the temperature in the vicinity of a preset value. One works, for instance, at a temperature of 750°C with a fluctuation of 20°C and a heating frequency of 20 minutes. One believes that this procedure can be useful in mineralizer reactions (Section 3.3) and in the preparation of single crystals (Section 3.4). Our first experiments gave positive results.