Chemical preparation I

Chemical transport reactions are used for synthesis, crystal growing and purification of compounds and elements. The technique entails the reversible conversion of nonvolatile elements and chemical compounds into volatile derivates. In such a reaction, a solid (or liquid) substance A(s) reacts with a transport reagent B(g) with formation of the gaseous substance AB(g). The reaction takes place in evacuated quartz ampoules heated in a tube furnace at a temperature gradient. At a temperature T1, the substance AB will be formed. The gaseous substance diffuses along the temperature gradient to the hotter or colder zone (T2) where it will decompose and A(s) in a pure state will be refined. Impurities will not either be taken in the gas phase and therefore remain in the arrear or they will not deposit at the higher temperature.

$$A(s) + B(g) \xrightarrow{T1} AB(g)$$
$$AB(g) \xrightarrow{T2} A(s) + B(g)$$

Transport reactions are rated according to the thermodynamics of the reaction. In *exothermic* reactions, the compound AB will tend to form at lower temperatures and decompose at higher temperatures. The purified substance A will be refined in the hotter part. In *endothermic* reactions, the forward reaction will take place from the colder to the hotter zone with the substance A refining at the colder zone. This follows the **Le Châtelier's principle**. If a chemical system at balance undergoes a change in temperature, the equilibrium will be shifted to counteract the inflicted change and a new equilibrium will be established.

The **van Arkel de Boer** process is used for a preparation of pure titanium with iodine as transporting agent. The crystals of pure titanium grow at the hottest part in the ampoule.

$$Ti + 2I_2 \xrightarrow{600°C} TiI_4$$
$$TiI_4 \xrightarrow{1200°C} Ti + 2I_2$$

The **Mond-process** applying carbon oxide as transporting agent is used for a conditioning of pure nickel in an exothermic reaction.

$$Ni + 4CO \xrightarrow{50–100°C} Ni(CO)_4$$
$$Ni(CO)_4 \xrightarrow{180–200°C} Ni + 4CO$$

Czochralski method: This method of crystal growth is used to obtain single crystals of semiconductors, metals or synthetic gemstones. The most important implication is the growth of large cylindrical boules of single crystal silicon. Silicon with only a few parts per million of impurities is melted down in a crucible made of quartz. A precisely oriented seed crystal, mounted on the end of a rotating rod, is placed in contact to the melt. The rod with the seed crystal is pulled slowly upwards and rotated at the same time counterclockwise, while the melt containing crucible is rotated clockwise. It is possible to extract a large cylindrical single crystal from the melt by precisely controlling the temperature gradient, the rate of pulling and the speed of rotation. The process is performed in an inert atmosphere such as argon and in an inert chamber of quartz.

Bridgman and Stockbarger methods: These two methods of single crystal growth are based on the solidification of a stoichiometric melt controlled by passing the melt through a temperature gradient. In the **Stockbarger method**, a melt containing ampoule is lowered in the furnace so that the melt crystallizes at the crossing to the colder oven part. The crystal orientation of the generated single crystal is controlled by a seed crystal placed in the colder part of the ampoule or through a single crystal formed by a constriction at the ampoule's end.

In the **Bridgman method**, using the same setup as in the Stockbarger method, the furnace is gradually cooled down so that the solidification starts at the cooler end of the oven.

Literature:

Anthony R. West: Basic Solid State Chemistry; second edition
Holleman-Wiberg: Inorganic Chemistry; 34th edition
Lecture notes: Advanced Inorganic Chemistry (Part 1) Basic Solid State Chemistry; WS 10/11(H.J. Deiseroth, V. Nickel)

Questions:

1. What are chemical transport reactions and wherefore are they used? Give an example of technical interest.
2. Name two methods of singe crystal growth and explain one method in detail!