stage sublimation at 437 °C is thus 1.70. Recent Japanese work indicates the possibility that the formidable engineering materials problems can be resolved. The key is to use a double-shelled reactor with the space between the shells pressurized to levels necessary to prevent stress corrosion of the inner chamber where the distillation is carried out.

See also: Zirconium Production; Metals Production: An Overview

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Halide Metallurgy

Halogens are used both in the primary extraction of metals from their ores and in the refining of metals to high purity. There are several reasons for this: (a) many metals have oxides that are very difficult to reduce, but halides that are not so refractory; (b) oxides of carbide-forming metals cannot be reduced by carbon or carbon monoxide; (c) halogens are less soluble in metals than oxygen and are more easily removed; and (d) the relatively high vapor pressures of many metal halides permit the use of distillation in the elimination of metallic impurities.

Some metals form several halides. Generally, the higher the valence, the more covalent is the compound, i.e., more volatile and easier to reduce to metal. For a given metal, the stability of its halides is proportional to the electronegativity of the halogens and increases in the order: iodide, bromide, chloride, fluoride. Care must be taken to avoid contact of the metal halides with water—the alkali and alkaline-earth halides are hygroscopic, and the transition-metal chlorides hydrolyze to produce oxides or oxychlorides and liberate hydrogen chloride gas. Thus, for the latter, subsequent dehydration can be achieved only by carbochlorination or by the use of powerful chlorinating agents such as thionyl chloride.

1. *Preparation of Metal Halides*

Anhydrous metal halides are prepared by several routes. The most common method, especially for chlorides, is halogenation of metal oxide in the presence of a reducing agent such as carbon, hydrogen or sulfur. This is typically performed in a shaft furnace. Alternative methods include halogenation of ferroalloys or carbides, and crystallization from aqueous solution. Crystallization works only for alkali chlorides and some alkaline-earth chlorides as the fluorides are typically insoluble in water and reactive metal halides hydrolyze.

Metal halides can be purified by several methods. In the case of volatile chlorides either fractional distillation or fractional reduction with hydrogen is used. In the case of water-soluble salts, dissolution and reprecipitation or recrystallization are feasible. Solvent extraction and ion exchange are also used.

2. *Reduction of Metal Halides*

There are four major methods of reducing metal halides to metal: metallothermic reduction, hydrogen reduction, thermal decomposition and electrolysis. Metallothermic reduction is the most common reduction method and is used primarily for producing reactive metals. The metal halide, either in solid or vapor form, is made to react with a metallic reducing agent, usually magnesium, calcium or sodium. In the Kroll process for titanium, titanium tetrachloride vapor reacts with magnesium in a closed reactor at 900 °C to produce solid titanium sponge and molten magnesium chloride. In the Hunter process, titanium tetrachloride vapor reacts with sodium at 900 °C to produce solid titanium sponge and molten sodium chloride. The metal sponge from both processes is subsequently melted to remove occluded salt. In the production of zirconium and hafnium there are similar processes in which the tetrachloride vapors are reacted with metallic magnesium, sodium or aluminum. Metallothermic reduction can also work when the metal halide is involatile. Uranium is produced by the reaction of uranium tetrafluoride powder with calcium metal chips in a calcium fluoride crucible at 1800 °C. There is no need for an inert atmosphere, as the molten calcium fluoride product makes this reaction self-fluxing. Beryllium is produced by the reaction of beryllium fluoride with metallic magnesium in a graphite crucible at 1300 °C. Calcium chloride is added as a fluxing agent.

Reduction of metal halides by hydrogen is another route to metal. Tungsten hexachloride borne by an argon carrier gas can be reacted with hydrogen in a two-zone furnace to produce tungsten powder of specified size. Process variables include the gas composition, hydrogen flow rate, and reaction temperature. Solid ferrous chloride has similarly been reduced with hydrogen to yield iron powder.

Both metallothermic reduction and hydrogen reduction of metal halides occur in primary metal extraction operations. In contrast, thermal decomposition of metal halides is used in the refining of metals. The prime example is the van Arkel–de Boer process for purifying titanium or zirconium. Impure metal is charged into a glass reactor where it is kept next to the reactor wall. The reactor, which contains a small quantity of iodine, is evacuated, sealed and heated to approximately 200 °C, at which temperature volatile titanium tetraiodide forms. A titanium filament which can be electrically heated is positioned in the center of the reactor. When molecules of titanium tetraiodide collide with the incandescent filament, they decompose to titanium metal which deposits on the filament, and to iodine gas which can again react with the titanium feedstock on the wall of the reactor.

A second example of refining by thermal decomposition of a metal halide is the subhalide process for aluminum. Aluminum trichloride vapor reacts with aluminum metal at 1200 °C to produce volatile aluminum monochloride. At temperatures below 700 °C the monochloride decomposes to give aluminum metal and trichloride vapor. In this way aluminum can be purified by transport out of an impure charge.

The final principal reduction method for metal halides is fused-salt electrolysis (see *Electrometallurgy*).

See also: High-Purity Metals; Metals Production: An Overview

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Halides

Halides (from the Greek *halos*, salt) are highly ionic salts of metals (M) and halogen gases (X_2). For the purpose of this article, halides are a class of nonmetallic, usually binary, inorganic solids incorporating F^-, Cl^-, Br^- or I^- ions in combination mainly with ions of group IA, IB or IIA metals. (Astatine is rare and highly radioactive, and astatides are therefore not covered in this article.)

The three most prominent members of this class are the alkali halides, the silver halides and the alkaline earth fluorides, all of which have been intensively studied since the early nineteenth century because of the relative purity of their naturally occurring mineral forms and the ease of preparation of synthetic analogues by crystallization from solution or the melt. These solids have in common a strong ionic bonding (binding energies $\sim 1\,\mathrm{MJ\,mol^{-1}}$), moderately high melting points ($T_m \sim 1000$ K), a wide electronic band gap (~8 eV), ionic conduction and easy cleavage on prominent crystallographic planes. They frequently serve as model systems for the study of relationships between bonding and structure, surface energy, epitaxy, ionic diffusion, point defects and color centers, solidification, plastic deformation and radiation damage. Commercial applications include use as optical windows, scintillator hosts, photographic and electron lithographic media, dosimeters, lasers, thin film substrates, fast ion conductors and geologically stable rock formations for storage of high-level solidified nuclear wastes.

Mixed-valence halides (e.g., $KMnF_3$, $KMgF_3$, $RbMgF_3$) have been investigated for their spectroscopic and in some cases magnetic properties. Other halides have been much less studied in the solid state and are not reviewed extensively here. Selected physical properties are listed in Table 1.

1. Structure

At normal temperature and pressure, seventeen of the twenty alkali halides, together with the silver halides AgCl and AgBr, crystallize with 6:6 coordination in the face-centered-cubic rocksalt structure. CsCl, CsBr and CsI crystallize with 8:8 coordination in the simple cubic CsCl structure. Cuprous halides and AgI are found in the 4:4-coordinated cubic zincblende and (at higher temperatures) hexagonal wurtzite structures. The alkaline earth fluorides CaF_2, SrF_2 and BaF_2, as well as $SrCl_2$, $BaCl_2$ and PbF_2, crystallize with 8:4 coordination in the face-centered-cubic fluorite structure, while MgF_2 is found with the (approximately) 6:3-coordinated rutile structure.

Most other MX_2 divalent metal halides crystallize in distorted versions of the rutile structure (e.g., $CaCl_2$), chain structures ($CuCl_2$) or layer structures ($CdCl_2$, CdI_2). BeF_2 and $BeCl_2$ have the 4:2-coordinated network structure of β-cristobalite at high temperature and can be produced in other SiO_2 polymorphs. Many trifluorides, like AlF_3, have a 6:2-coordinated ReO_3 structure in which MF_6 octahedra are centered at the corners of a cubic unit cell. Other trivalent metal halides have higher-coordination three-dimensional structures or layer structures. Mixed-valence halides like $KMgF_3$ have the cubic perovskite structure with 12:6:6 coordination.

Extensive and variously successful attempts have been made to account for choice of structure, based on the lattice energy of a point ion model with various choices for the form of ion core repulsion and corrections for polarizability. The best approach to date appears to be the use of the shell model to accommodate polarization and a set of empirical potentials matched to elastic and dielectric properties (Catlow et al. 1977). Computer codes embodying this approach (Catlow 1980) have been utilized to generate the best model information on point and