Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, MAGNESIUM

1. Magnesium Fluoride

1.1. Properties

Magnesium fluoride [7783-40-6], MgF_2, is a fine white crystalline powder with low chemical reactivity. This relative inertness makes possible some of its uses, eg, stable permanent films to alter light transmission properties of optical and electronic materials. The reaction with sulfuric acid is so sluggish and incomplete that magnesium fluoride is not a suitable substitute for calcium fluoride in manufacturing hydrogen fluoride. Magnesium fluoride resists hydrolysis to hydrogen fluoride up to 750°C (1). Bimetallic fluorides, such as $KMgF_3$ [28042-61-7], are formed on fusion of MgF_2 alkali metal and ammonium fluorides (2). Chemical and physical properties are listed in Table 1. MgF_2 is birefringent and only mildly affected by high energy radiation, making possible optics for the uv region.

1.2. Manufacture

Magnesium fluoride is manufactured by the reaction of hydrofluoric acid and magnesium oxide or carbonate:

$$MgO + 2\ HF \longrightarrow MgF_2 + H_2O$$

$$MgCO_3 + 2\ HF \longrightarrow MgF_2 + CO_2 + H_2O$$

Formation of a gelatinous precipitate that is difficult to filter can be avoided by addition of magnesium oxide to the acid solution. In order to increase particle size it is often necessary to keep the solution hot for several hours; however, this problem is avoided by heating an intimate mixture of ammonium bifluoride with magnesium carbonate to 150–400°C (11). Particles of MgF_2 similar in size to those of the magnesium carbonate are obtained.

$$MgCO_3 + NH_4HF_2 \xrightarrow{150-400^\circ C} MgF_2 + NH_3 + CO_2 + H_2O$$

The same results are obtained by adding magnesium carbonate to an aqueous solution of ammonium bifluoride and ammonium hydroxide and warming to 60°C (12). The resulting precipitate is ammonium magnesium fluoride [35278-29-6] which settles rapidly.

$$MgCO_3 + 3\ NH_4F\ (aq) \longrightarrow NH_4MgF_3 + (NH_4)_2\,CO_3$$

Table 1. Chemical and Physical Properties

Property	Value	Reference
melting point, °C	1263	3
boiling point, °C	2227	3
standard heat of formation, kJ/mol[a]	−112.4	4
standard entropy of formation, J/(mol·K)[a]	178	5
heat of fusion, kJ/mol[a]	58.2	3
heat of vaporization, kJ/mol[a]	264	5
lattice energy, kJ/mol[a]	2920	5
heat capacity, 25°C, J/(mol·K)[a]	61.59	3
free energy of solution, kJ/mol[a]	40.2	5
density, g/cm^3	3.127	6
index of refraction[b]		
n_o[c]	1.37770	7
n_e	1.38950	7
crystalline form (sellaite)	tetragonal	6
a, nm	0.4623	
c, nm	0.3052	
solubility, g/100 g of solvent		
water, 25°C	0.013	8
hydrogen fluoride, 12°C	0.025	9
acetic acid, 25°C	0.681	10

[a]To convert kJ to kcal, divide by 4.184.
[b]*o*, ordinary; *e*, extraordinary.
[c]At 589 nm.

$$NH_4MgF_3 \xrightarrow[4\ h]{620^\circ C} MgF_2 + NH_3 + HF$$

Magnesium fluoride is a by-product of the manufacture of metallic beryllium and uranium. The beryllium or uranium fluorides are intimately mixed with magnesium metal in magnesium fluoride-lined crucibles. On heating, a Thermite-type reaction takes place to yield the desired metal and MgF_2 (13). Part of the magnesium fluoride produced in this reaction is then used as a lining for the crucibles used in the process.

$$BeF_2 + Mg \longrightarrow Be + MgF_2$$

A commercial grade of magnesium fluoride containing approximately 96–98% MgF_2 is manufactured by Advance Research Chemicals and the Bicron Co. in the United States. Imported technical grades suitable for fluxes containing 94–96% magnesium fluoride are available from Atomergic Chemetals Co., Fine Chemical Co., and Magnesium Elektron.

Magnesium fluoride optical crystals are made by hot-pressing (14) high quality MgF_2 powder. The optical quality powder is made by the NH_4HF_2 method described (11) or by reaction of magnesium bicarbonate and hydrofluoric acid (15). Lead fluoride can also be used in purification of MgF_2 for optical crystals (16). Such optical crystals are manufactured by Bicron Co.

1.3. Toxicity

The lethal dose of MgF_2 to guinea pigs by ingestion is 1000 mg/kg (17).

1.4. Uses

Established uses of magnesium fluoride are as fluxes in magnesium metallurgy and in the ceramics industry. A proposed use is the extraction of aluminum from arc-furnace alloys with Fe, Si, Ti, and C (18). The molten alloy in reacting with magnesium fluoride volatilizes the aluminum and magnesium which are later separated above the melting point of MgF_2. A welding (qv) flux for aluminum (19) as well as fluxes for steel (20) contain MgF_2.

Optical windows of highly purified magnesium fluoride which transmit light from the vacuum ultraviolet (140 nm) into the infrared (7) are recommended for use as ultraviolet optical components for use in space exploration.

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