Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, LEAD

1. Lead Difluoride

Lead difluoride [7783-46-2], PbF_2, has the highest melting and boiling points among all the dihalides of lead. Two colorless crystalline forms are known. The α-PbF_2 is orthorhombic in structure and is stable at ordinary temperatures. Upon heating to 200°C it transforms to the cubic β-form. Table 1 lists some of the physical properties of PbF_2.

PbF_2 is readily prepared by the action of hydrogen fluoride on lead hydroxide, lead carbonate, or α-lead oxide. It can also be obtained by precipitation from lead nitrate or lead acetate solutions using potassium fluoride, ammonium fluoride, or ammonium bifluoride.

PbF_2 exhibits very good electrical insulating properties and optical transparency. It is thus used in a variety of glass (qv) such as sealing glass (1), low melting glass (2), near infrared absorbing glass for fiber optics (qv) (3), weather-resistant glass (4, 5), and glass for active optical fibers (6). It is also used in printing, photography (qv), brazing, scintillation counters (7), dielectric interference filters (8), as a mild fluorinating reagent, as a source material for PbF_4, and as an ingredient in lead–acid batteries (qv) (9).

High purity lead difluoride is available from Advance Research Chemicals, Aldrich Chemicals, Johnson/Matthey, Atomergic, Cerac, and other suppliers in the United States. The U.S. annual consumption varies between 500 to 2500 kg/yr. The 1993 price varied between \$10–20/kg.

2. Lead Tetrafluoride

Like all the lead tetrahalides, lead tetrafluoride [7783-59-7],PbF_4, is very reactive. It is relatively the most stable halide, however. PbF_4 is a white crystalline powder which is highly moisture sensitive, turning yellowish brown in moist air owing to hydrolysis. It should be handled in a dry box or under an atmosphere of dry nitrogen. Properties for PbF_4 are in Table 1.

PbF_4, produced by various routes including the *in situ* species, is a very effective fluorinating agent and also an oxidizing agent. It is classified as a hard fluorinating agent (10), replacing hydrogen with fluorine or adding fluorine to double bonds of both halogenated and hydrocarbon olefins to produce difluorocarbons (11, 12).

$$CCl_2{=}CCl_2 + PbF_4 \longrightarrow CCl_2FCCl_2F + PbF_2 \qquad (1)$$

$$CF_3CCl{=}CCl_2 + PbF_4 \longrightarrow CF_3CClFCCl_2F + PbF_2 \qquad (2)$$

Table 1. Physical Properties of Lead Fluorides

Property	PbF_2	PbF_4
mol wt	245.19	283.2
density, g/cm^3	8.24	6.7
melting point, °C	855	600
boiling point, °C	1290	decomposes
solubility, g/100 g		
water	0.0641	[a]
anhydrous HF	2.628	
ΔH_f, kJ/mol[b]	−677	
ΔG_f, kJ/mol[b]	−631	
C_p, J/(mol·K)[b]	72.3	
S, J/(mol·K)[b]	−113	

[a] Material hydrolyzes to PbO_2 and HF.
[b] To convert J to cal, divide by 4.184.

$$CHCl{=}CHCl + PbF_4 \longrightarrow CHClFCHClF + PbF_2 \qquad (3)$$

It is also used in the preparation of biologically active steroids where the fluorine is added in a cis configuration to the double bond (13, 14).

Lead fluorides are highly toxic and should be handled with great care. The ACGIH adopted toxicity value for lead compounds as Pb is TWA 0.15 mg/m^3 and for fluorides as F^- 2.5 mg/m^3. PbF_4 is prepared by the action of elemental fluorine on very dry PbF_2 at 280–300°C (15).

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