Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, RHENIUM

1. Rhenium Hexafluoride

Rhenium hexafluoride [10049-17-9], ReF_6, is a pale yellow solid at 0°C, but a liquid at ambient temperature. In the presence of moisture it hydrolyzes rapidly forming HF, ReO_2, and $HReO_4$ (see Rhenium and rhenium compounds). It is not safe to storeReF_6 in a glass trap or glass-lined container. Leaks in the system can initiate hydrolysis and produce HF. The pressure buildup causes the system to burst and an explosion may result.

1.1. Properties

Some physical properties of ReF_6 are mol wt, 300.19; mp, 18.5°C; bp, 33.7°C; solubility in HF, 52.5 g/100 g; specific gravity, 3.58; and vapor pressure at 20.3°C, 61 kPa (458 mm Hg). The transition point has been reported as −3.45 (1) and −1.9°C (2). The compound can be handled in dry metal vacuum lines made of copper, nickel, stainless steel, or Monel. It forms a passive fluoride film on the surface which protects these metals from further corrosion. Reaction with nitric oxide yields nitrosonium hexafluororhenate [60447-76-9], $NOReF_6$ (3), and with potassium fluoride yields potassium octafluororhenate [57300-90-0], K_2ReF_8 (4). Reaction with alkali metal iodides dissolved in SO_2 results in the reduction to rhenium(IV) complex salts, M_2ReF_6 (M = Na [12021-61-3], K [16962-12-2], Rb [16962-13-3], and Cs [16962-14-4]) (5).

Rhenium hexafluoride is readily prepared by the direct interaction of purified elemental fluorine over hydrogen-reduced, 300 mesh (ca 48 μm) rhenium powder at 120°C. The reaction is exothermic and temperature rises rapidly. Failure to control the temperature may result in the formation of rhenium heptafluoride. The latter could be reduced to rhenium hexafluoride by heating with rhenium metal at 400°C.

Rhenium hexafluoride is used for the deposition of rhenium metal films for electronic, semiconductor, laser parts (6–8), and in chemical vapor deposition (CVD) processes which involve the reduction of ReF_6 by hydrogen at elevated (550–750°C) temperatures and reduced ($<$101.3 kPa (1 atm)) pressures (9, 10).

Rhenium hexafluoride is a costly (ca $3000/kg) material and is often used as a small percentage composite with tungsten or molybdenum. The addition of rhenium to tungsten metal improves the ductility and high temperature properties of metal films or parts (11). Tungsten–rhenium alloys produced by CVD processes exhibit higher superconducting transition temperatures than those alloys produced by arc-melt processes (12).

Rhenium hexafluoride (99.5% pure) is commercially available from Advance Research Chemicals, Atomergic, Atochem, Spectra Gases, and Matheson Gas of the United States, Fluorochem of the United Kingdom, and other sources. The 1993 price for small quantities varied from $3000 to $3500/kg. Larger quantities were available at $2000 to $2500/kg depending on the price of rhenium metal. U.S. production is less than 100 kg/yr. Because of its high irritating and corrosive nature it is classified as corrosive, poisonous liquid and shipped in steel, stainless steel, or Monel cylinders. Upon exposure to air it hydrolyzes producing HF fumes that are corrosive to the lower respiratory tract, skin, and eyes. Prolonged exposure to fumes may cause pulmonary edema. ACGIH (1992–1993) adopted TLV for fluorides as F^- is 2.5 mg/m^3; therefore great care should be taken

Table 1. Rhenium Oxyfluorides[a]

Compound	$ReOF_5$	ReO_2F_3	ReO_3F	$ReOF_4$	$ReOF_3$
preparative route	$ReO_2 + F_2$	$ReO_2 + F_2$	$KReO_4 + IF_5$	$ReF_6 + M(CO)_x$	$ReF_6 + M(CO)_x$
color	cream	pale yellow	yellow	blue	black
mp, °C	40.8[b]	90	71	107.8[b]	>200

[a] Refs. (14–16).
[b] Transition point.

while handling ReF_6. Personnel working with this material should use vacuum lines or closed systems located in a chemical hood. All precautions must be taken to avoid breathing of vapors or contact with skin.

2. Other Rhenium Fluoride Compounds

Rhenium heptafluoride [17029-21-9], ReF_7, is obtained by the direct interaction of elemental fluorine with hydrogen-reduced rhenium powder at 400°C and slightly over atmospheric pressure of fluorine. It is a pale yellow solid, mol wt 319.19; mp, 48.3°C; and bp, 73.7°C.

Rhenium pentafluoride [30937-52-1], ReF_5, is obtained along with rhenium tetrafluoride [15192-42-4], ReF_4, when reduction of ReF_6 is carried out with metal carbonyls (qv). ReF_5 is a greenish yellow solid with mp 48°C. Its ready thermal decomposition and magnetic properties suggest that it may be $ReF^{+}{}_4ReF^{-}{}_6$ (13). ReF_4, best prepared by the reduction of rhenium hexafluoride with hydrogen at 200°C, is a pale blue solid melting at 124.5°C and boiling at 795°C.

Rhenium also forms several important oxyfluorides: rhenium oxytetrafluoride [17026-29-8], $ReOF_4$; rhenium oxypentafluoride [23377-53-9], $ReOF_5$; rhenium dioxytrifluoride [57246-89-6], ReO_2F_3; and perrhenyl fluoride[25813-73-4], ReO_3F. All are solids at room temperature. Properties are summarized in Table 1.

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