Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, ARSENIC

Arsenic forms the binary compounds arsenous trifluoride and arsenic pentafluoride, as well as a series of compounds and the acid of the very stable hexafluoroarsenate ion.

Great care should be exercised in the handling and use of all arsenic compounds (qv) because NIOSH has determined inorganic arsenic to be a carcinogen and OSHA considers inorganic arsenic to be a cancer hazard. The OSHA permissible exposure limit is 10 μg/m^3, averaged over any 8-h period. The OSHA action level is 5 μg/m^3, averaged over any 8-h period. The OSHA limits have the force of law and are much lower than the 0.2 mg/m^3 of ACGIH.

1. Arsenous Fluoride

Arsenous fluoride [7784-35-2], AsF_3, is a colorless liquid, mp = $-5.95°C$, bp = $57.13°C$ at 99 kPa (742.5 mm Hg) (1), and sp gr = 2.67, having a standard enthalpy of formation of -858.1 kJ/mol (-205.1 kcal/mol) (2). Arsenic(III) fluoride can be prepared by fluorination of arsenous oxide using sulfuric acid and calcium fluoride (3), or using hydrofluoric acid or fluorosulfuric acid; from thermal decomposition of $AsBr_4AsF_6$ (4); from the fluorination of gallium arsenide using F_2 or NF_3 (5); from As_2O_3, CaF_2, and concentrated H_2SO_4 (6); from disproportionation of graphite intercalated compounds of AsF_5 (7); from the reaction of arsenous trichloride with NaF at 300°C in the presence of $ZnCl_2$ or KCl (8), and from the fluorination of arsenous trichloride with antimony trifluoride or zinc fluoride (9).

It is used as a fluorinating reagent in semiconductor doping, to synthesize some hexafluoroarsenate compounds, and in the manufacture of graphite intercalated compounds (10) (see Semiconductors). AsF_3 has been used to achieve $>8\%$ total area simulated air-mass 1 power conversion efficiencies in Si *p-n* junction solar cells (11) (see Solar energy). It is commercially produced, but usage is estimated to be less than 100 kg/yr.

2. Arsenic Trifluoride Oxide

Arsenic trifluoride oxide [15120-14-6], $AsOF_3$, has been reported to be produced by the uv photolysis of O_3 or HOF in the presence of AsF_3 (12, 13).

3. Arsenic Pentafluoride

Arsenic pentafluoride [7784-36-3], AsF_5, melts at $-79.8°C$ and boils at $-52.8°C$ (14). At the boiling point the liquid has a density of 2.33 g/mL. The standard enthalpy of formation is -1237 kJ/mol (-295.6 kcal/mol), and the average bond strength is 387 kJ/mol (92.4 kcal/mol), compared to 484.1 kJ/mol (115.7 kcal/mol) for AsF_3 (15).

Arsenic pentafluoride can be prepared by reaction of fluorine and arsenic trifluoride or arsenic; from the reaction of NF_3O and As (16); from the reaction of $Ca(FSO_3)_2$ and H_3AsO_4 (17); or by reaction of alkali metal or alkaline-earth metal fluorides or fluorosulfonates with H_3AsO_4 or H_2AsO_3F (18).

It is used as a fluorinating reagent and in syntheses of some hexafluoroarsenate compounds. Arsenic pentafluoride is also used to dope semiconductors (19); to produce conductive polymers (20, 21); and in conducting-oriented fibers (22). Arsenic pentafluoride has been found to react with graphite to form AsF_5–graphite intercalation compounds (23) having electrical conductivity as high as that of silver (24, 25). Arsenic pentafluoride is produced commercially and usage is estimated to be less than 100 kg/yr.

4. Hexafluoroarsenic Acid and the Hexafluoroarsenates

The $AsF^{-};_6$ ion is very stable toward hydrolysis in aqueous solution. It is not hydrolyzed by boiling a strongly basic solution almost to dryness (26), although it is hydrolyzed in sulfuric acid (27) or in boiling perchloric acid (26). The hydrolysis of $AsF^{-};_6$ in concentrated sulfuric acid (27) and in base (28) at 193–222°C is first order in $AsF^{-};_6$. The hydrolysis of $AsF^{-};_6$ in alkaline solution is slower than either $PF^{-};_6$ or $SbF^{-};_6$.

Hexafluoroarsenic acid [17068-85-8] can be prepared by the reaction of arsenic acid with hydrofluoric acid or calcium fluorosulfate (29) and with alkali or alkaline-earth metal fluorides or fluorosulfonates (18). The hexafluoroarsenates can be prepared directly from arsenates and hydrofluoric acid, or by neutralization of $HAsF_6$. The reaction of 48% HF with potassium dihydrogen arsenate(V), KH_2AsO_4, gives potassium hydroxypentafluoroarsenate(V) [17068-84-7], $KAsF_5OH$, which hydrolyzes rapidly in water solution (26). Anhydrous HF reacts with KH_2AsO_4 or $KAsF_5OH$ to produce $KAsF_6$ [17029-22-0]. O_2AsF_6 [12370-43-3] can be prepared from the reaction of OF_2 and AsF_5 or a mixture of O_2, F_2, and AsF_5 (30). Reactions of $XeF(AsF_6)$ and water give $H_2OF(AsF_6)$ which reacts with SF_4 to produce $OSF_3(AsF_6)$ and with ClF_3 to produce $OClF_2AsF_6$ (31). The compound $SCl_3{}^{\cdot}AsF_6$ has also been reported (32).

Because of the special stability of the hexafluoroarsenate ion, there are a number of applications of hexafluoroarsenates. For example, onium hexafluoroarsenates (33) have been described as photoinitiators in the hardening of epoxy resins (qv). Lithium hexafluoroarsenate [29935-35-1] has been used as an electrolyte in lithium batteries (qv). Hexafluoroarsenates, especially alkali and alkaline-earth metal salts or substituted ammonium salts, have been reported (34) to be effective as herbicides (qv). Potassium hexafluoroarsenate [17029-22-0] has been reported (35) to be particularly effective against prickly pear. However, environmental and regulatory concerns have severely limited these applications.

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