

FLUORINE COMPOUNDS, INORGANIC, POTASSIUM

The two stable salts of potassium and fluorine of commercial significance are the normal fluoride [7789-23-3], KF, and potassium bifluoride [7789-29-9], KHF_2 .

1. Potassium Fluoride

1.1. Properties

Anhydrous potassium fluoride [7789-23-3] is a white hygroscopic salt that forms two hydrates, $\text{KF} \cdot 2\text{H}_2\text{O}$ [13455-21-5] and $\text{KF} \cdot 4\text{H}_2\text{O}$ [34341-58-7]. The tetrahydrate exists at temperatures below 17.7°C. The dihydrate is stable at room temperature and starts to lose water above 40°C. Temperatures on the order of 250–300°C are required to remove the last few percent of water in a reasonable period of time. Potassium fluoride does not pyrohydrolyze at temperatures as high as 1000°C (1). Chemical and physical properties of KF are summarized in Table 1.

Halogen exchange with KF is not successful in acetic acid (10). Hydrogen bonding of the acid hydrogen with the fluoride ion was postulated to cause acetate substitution for the halide; however, the products of dissolved KF in acetic acid are potassium acetate and potassium bifluoride (11). Thus KF acts as a base rather than as a fluorinating agent in acetic acid.

1.2. Manufacture

Commercial KF is manufactured from potassium hydroxide and hydrofluoric acid followed by drying in a spray dryer or flaking from a heated drum. The KF assay is typically 97–99%; impurities are $\text{KF} \cdot 2\text{H}_2\text{O}$ and either potassium carbonate or potassium bifluoride. The 1992 price of the anhydrous salt was \$4.68/kg and that of the reagent-grade dihydrate ranged from \$8–\$14/kg. Potassium fluoride can be purified by passing anhydrous HF through the melt (12).

1.3. Toxicology

By ingestion, the lethal dose of potassium fluoride in guinea pigs is 250 mg/kg body weight. The LD_{50} orally for rats is 245 mg/kg body weight (13). Ingestion of potassium fluoride may cause vomiting, abdominal pains, and diarrhea.

1.4. Uses

Potassium fluoride is used in the manufacture of silver solder fluxes and in fluxes for various metallurgical operations (see Solders and brazing filler metals). In tin deposition from halogen plating baths, KF is used to complex tetravalent tin to form K_2SnF_6 [16893-93-9] which may be filtered from the solution (see Electroplating)

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Table 1. Physical and Chemical Properties of Potassium Fluoride

Property	Value	Reference
melting point, °C	857	2
boiling point, °C	1505	2
specific gravity at 25°C	2.48	2
solubility, g/100 g		
in H ₂ O, 25°C	49.6	3
in liquid HF, 8°C	36.5	4
in acetic acid, 25°C	28	5
in methanol, 25°C	2.3	6
standard heat of formation, kJ/mol ^a		
KF	−567.4	2
KF·2H ₂ O	−1159	7
heat of fusion, kJ/mol ^a	28.2	2
heat of vaporization, kJ/mol ^a	173	7
heat of dehydration, KF·2H ₂ O, kJ/mol ^a	58.2	8
entropy at 25°C, J/(mol·K) ^a	66.6	2
lattice energy, kJ/mol ^a	813.8	9
specific heat, J/(kg·K) ^a		
at 0°C	833	2
at 50°C	854	2

^aTo convert kJ to kcal, divide by 4.184.

(14). Highly purified KF is formed into single crystals by the Stockbarger process (15). The principal use of the crystals is in the studies of fundamental properties and defects in alkali halide crystals used in introducing fluorine in organic synthesis.

For many types of replacement of halogens by fluorine in organic compounds, KF is the most frequently used fluoride. As a fluorinating agent, KF must be as anhydrous as possible and very finely divided. The potassium chloride or bromide by-products from reactions with organic chlorides or bromides deposit on the potassium fluoride crystal surfaces, significantly retarding the reaction. Polar solvents such as acetonitrile, dimethyl sulfoxide, or formamide, and rapid stirring are useful in overcoming this drawback. Ball-milling the reaction mixture is also helpful in speeding up the reaction. This fluorination process is used commercially in the manufacture of sodium fluoroacetate, a useful rat poison sold as “1080” (see Fluorine compounds, organic–fluorinated acetic acid). An alkyl haloacetate is converted to an alkyl fluoroacetate which is then hydrolyzed using sodium hydroxide to the final product. Similarly, fluoroacetamide, a systemic insecticide, is made from chloroacetamide. Organic fluorides (16) that may be prepared from corresponding bromides or chlorides using potassium fluoride include monofluoroalkanes; α -fluoroesters, -ethers, and -alcohols; acyl fluorides; sulfonyl fluorides; and 1-fluoro-2,4-dinitrobenzene. Potassium fluoride behaves as a base when used as a catalyst for reactions such as dehydrohalogenation (17), Michael addition (18), and the Knoevenagel reaction (19). Polyurethane foams can be formed when KF is used as a catalyst for the reaction of adiponitrile carbonate and a polyester polyol (20) (see Urethane polymers).

2. Potassium Bifluoride

2.1. Properties

Other names for potassium bifluoride are potassium hydrogen difluoride and potassium acid fluoride. This white crystalline salt is a soft, waxy solid. The crystal forms of potassium bifluoride are tetragonal and cubic (21). The bifluoride ion in KHF₂ averages 0.2292 nm between fluoride ions in the F–H–F group (22). At

Table 2. Properties of Potassium Bifluoride, KHF₂

Property	Value	Reference
melting point, °C	238.8	23
specific gravity	2.37	24
solubility in H ₂ O, 20°C, g/100 g	39.2	
crystal transition temperature, °C	196.7	23
standard heat of formation, kJ/mol ^a	-920.4	7
heat of fusion, kJ/mol ^a	6.6	23
heat of dissociation to KF + HF, 226.8°C, kJ/mol ^a	77.5	24
entropy, 25°C, J/(mol·K) ^a	104.3	7
heat capacity, C _p , 25°C, J/(mol·K) ^a	76.86	7
lattice energy, kJ/mol ^a	641.8	24

^aTo convert kJ to kcal, divide by 4.184.

elevated temperatures, potassium bifluoride exhibits an appreciable vapor pressure of HF. At 440°C, KHF₂ is decomposed completely to KF and HF; this decomposition is a convenient means of obtaining very pure HF. Other chemical and physical properties are summarized in Table 2.

2.2. Manufacture

Potassium bifluoride is produced from potassium hydroxide or potassium carbonate and hydrofluoric acid. The concentrated solution is cooled and allowed to crystallize. The crystals are separated centrifugally and dried. The commercial product consists typically of 99.7% KHF₂ and 0.2% KF. Potassium bifluoride is available in the United States in 180-kg drums at \$4.04/kg (1992).

2.3. Toxicology and Handling

The lethal dose by ingestion in guinea pigs is 150 mg/kg body weight (13). The TLV for KHF₂ is 2.5 mg/m³ (25). Potassium bifluoride crystals may break down to a fine white powder that is readily airborne. In this form, the salt is quite irritating to the nasal passages, eyes, and skin. Therefore, the hands and eyes should be protected and acid dust masks should be worn while handling, as an acid fluoride KHF₂ can cause superficial hydrofluoric acid-type burns. Areas of skin that have been in contact with potassium bifluoride should be washed as soon as possible with mildly alkaline soaps or borax-containing hand cleaners. If there has been contact with the eyes, they should be washed well with water and a physician should be consulted.

2.4. Uses

A primary use for potassium bifluoride is in the electrolyte for cells in fluorine manufacture (26). Sufficient hydrogen fluoride is dissolved with KHF₂ to bring the total HF content up to 40–42 wt %. This mixture approximates the formula KF·2HF; it is molten at 90°C, the operating temperature of the cell. Fluxes for a wide variety of metal joining applications utilize KHF₂, usually in combination with potassium pentaborate, boric acid, and other fluorides and chlorides such as ZnCl₂ (27). Solutions of KHF₂ and citric acid are used to etch aluminum prior to coating with an acrylic copolymer emulsion; this opaque white coating resists chipping and is useful for automotive, architectural, and decorative applications (28). Tetrahydrofuran is polymerized to poly(tetramethylene glycol) with fuming sulfuric acid and potassium bifluoride (29).

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JOHN R. PAPCUN
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