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FLUORINE COMPOUNDS, INORGANIC, AMMONIUM

Two well-known salts of ammonia (qv) are the normal ammonium fluoride [12125-01-8], NH_4F, and ammonium bifluoride [1341-49-7], NH_4HF_2; the latter is sometimes named ammonium acid, or hydrogen difluoride. Much of the commercial interest in the ammonium fluorides stems from their chemical reactivity as less hazardous substitutes for hydrofluoric acid.

1. Ammonium Fluoride

Ammonium fluoride is a white, deliquescent, crystalline salt. It tends to lose ammonia gas to revert to the more stable ammonium bifluoride. Its solubility in water is 45.3 g/100 g of H_2O at 25°C and its heat of formation is -466.9 kJ/mol (-116 kcal/mol). Ammonium fluoride is available principally as a laboratory reagent. If it is needed in large quantities, one mole of aqueous ammonia can be mixed with one mole of the more readily available ammonium bifluoride (1).

2. Ammonium Bifluoride

2.1. Properties

Ammonium bifluoride, NH_4HF_2, is a colorless, orthorhombic crystal (2). The compound is odorless; however, less than 1% excess HF can cause an acid odor. The salt has no tendency to form hydrates yet is hygroscopic if the ambient humidity is over 50%. A number of chemical and physical properties are listed in Table 1.

2.1.1. Corrosion

Ammonium bifluoride dissolves in aqueous solutions to yield the acidic bifluoride ion; the pH of a 5% solution is 3.5. In most cases, NH_4HF_2 solutions react readily with surface oxide coatings on metals; thus NH_4HF_2 is used in pickling solutions (see Metal surface treatments). Many plastics, such as polyethylene, polypropylene, unplasticized PVC, and carbon brick, are resistant to attack by ammonium bifluoride.

2.2. Manufacture

Anhydrous ammonium bifluoride containing 0.1% H_2O and 93% NH_4HF_2 can be made by dehydrating ammonium fluoride solutions and by thermally decomposing the dry crystals (7). Commercial ammonium bifluoride, which usually contains 1% NH_4F, is made by gas-phase reaction of one mole of anhydrous ammonia and two moles of anhydrous hydrogen fluoride (8); the melt that forms is flaked on a cooled drum. The cost of the material in 1992 was $1.48/kg.

Production of bifluoride from fluoride by-products from the phosphate industry (9) has had little if any commercial significance.

Table 1. Properties of Ammonium Bifluoride, NH_4HF_2

Property	Value	Reference
melting point, °C	126.1	3
boiling point, °C	239.5	3
index of refraction, n_D	1.390	3
solubility at 25°C, wt %		
water	41.5	3
90% ethanol	1.73	3
specific gravity	1.50	3
standard heat of formation, kJ/mol[a]	−798.3	4
heat of fusion, kJ/mol[a]	19.1	4
heat of vaporization, kJ/mol[a]	65.3	4
heat of solution, kJ/mol[a]	20.3	4
heat of dissociation,[b] kJ/mol[a]	141.4	4
heat capacity, C_p, J/(mol·K)[a] at 25°C	106.7	4
vapor pressure,[c] $\log P_{Pa} = a - bT^{-1}$		
153–207°C	$a = 11.72$, $b = 3370$	5
207–245°C	$a = 9.38$, $b = 2245$	5
oral LD (guinea pig), mg/kg	150	6

[a] To convert kJ to kcal, divide by 4.184.

[b] $NH_4HF_2 \longrightarrow NH_3 + 2\,HF\cdot$

[c] To convert Pa to mm Hg, multiply by 7.5×10^{-3}.

2.3. Precautions in Handling

Ammonium bifluoride, like all soluble fluorides, is toxic if taken internally. Hydrofluoric acid burns may occur if the material comes in contact with moist skin. Ammonium bifluoride solutions should be thoroughly washed from the skin with mildly alkaline soap as soon as possible; however, if contact has been prolonged, the affected areas should be soaked with 0.13% solution of Zephiran chloride, or 0.2% Hyamine 1622 (Lonza, Inc.) or calcium gluconate, the treatment recommended for hydrofluoric acid burns. If any of these solutions come in contact with the eyes, they should be washed with water for at least 10 min and a physician should be consulted.

2.4. Applications

Ammonium bifluoride solubilizes silica and silicates by forming ammonium fluorosilicate [16919-19-0], $(NH_4)_2SiF_6$. Inhibited 15% hydrochloric acid containing about 2% ammonium bifluoride has been used to acidize oil wells in siliceous rocks to regenerate oil flow (10) (see Petroleum). Ammonium fluoride solution is made on-site near the well bore from ammonium bifluoride and ammonia and mixed with methyl formate to prevent rapid consumption of most of the HF (11). The use of ammonium bifluoride is important in locations where dissolved silicates foul boiler tubes with scale that cannot be removed using usual cleaning aids (12). Ammonium bifluoride is also used as an etching agent for silicon wafers.

Rapid frosting of glass is accomplished in a concentrated solution of ammonium bifluoride and hydrofluoric acid with nucleating agents that assure uniform frosts (13). A single dip in an aqueous solution of NH_4HF_2, HF, and sorbitol at $<20°C$ for less than 60 s produces the low specular-reflecting finish on television face plates and on (qv) for picture framing (14). Treating glass, eg, often badly weathered window panes, with 2–5% solutions of ammonium bifluoride results in a polishing effect. Glass ampuls for parenteral solutions (15) and optical lenses (16) are best cleaned of adhering particulate matter in dilute ammonium bifluoride solutions.

Ammonium bifluoride is used as a sour or neutralizer for alkalies in commercial laundries and textile plants. Treatment also removes iron stain by forming colorless ammonium iron fluorides that are readily rinsed from the fabric (17).

Ammonium fluorides react with many metal oxides or carbonates at elevated temperatures to form double fluorides; eg,

$$2\ NH_4HF_2 + BeO \xrightarrow{-H_2O} (NH_4)_2BeF_4 \xrightarrow{\Delta} BeF_2 + 2\ NH_3 + 2\ HF$$

The double fluorides decompose at even higher temperatures to form the metal fluoride and volatile NH_3 and HF. This reaction produces pure salts less likely to be contaminated with oxyfluorides. Beryllium fluoride[7787-49-7], from which beryllium metal is made, is produced this way (18) (see Beryllium and beryllium alloys). In pickling of stainless steel and titanium, NH_4HF_2 is used with high concentrations of nitric acid to avoid hydrogen embrittlement. Ammonium bifluoride is used in acid dips for steel (qv) prior to phosphating and galvanizing, and for activation of metals before nickel plating (19, 20). Ammonium bifluoride also is used in aluminum anodizing formulations. Ammonium bifluoride is used in treatments to provide corrosion resistance on magnesium and its alloys (21). Such treatment provides an excellent base for painting and good abrasion resistance, heat resistance, and protection from atmospheric corrosion. A minor use for ammonium bifluoride is in the preservation of wood (qv) (22).

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