Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, NICKEL

1. Nickel Fluoride Tetrahydrate

Nickel fluoride tetrahydrate [13940-83-5], $NiF_2{\cdot}4H_2O$, and its anhydrous counterpart, nickel fluoride [10028-18-9], NiF_2, are the only known stable binary compounds of nickel and fluorine. The former is a greenish light yellow crystal or powder prepared by the addition of nickel carbonate to 30–50% aqueous HF solution. The nickel fluoride formed first goes into solution and then precipitates out as the tetrahydrate as the concentration of nickel fluoride increases and that of HF decreases. When the addition of nickel is complete, the solution and the precipitates are dried at 75–100°C until all the water is expelled. The tetrahydrate has high solubility in aqueous HF, eg, 13.3 wt % in 30% HF. It is slightly soluble in water and insoluble in alcohol and ether.

Historically, the annual consumption of nickel fluoride was on the order of a few metric tons. Usage is dropping because nickel fluoride is listed in the EPA and TSCA's toxic substance inventory. Nickel fluoride tetrahydrate is packaged in 200–500-lb (90.7–227-kg) drums and the 1993 price was $22/kg. Small quantities for research and pilot-plant work are available from Advance Research Chemicals, Aldrich Chemicals, Johnson/Matthey, Pfaltz and Bauer, PCR, and Strem Chemicals of the United States, Fluorochem of the United Kingdom, and Morita of Japan.

2. Nickel Fluoride, Anhydrous

Anhydrous nickel fluoride, a light yellow colored powder, is prepared by the action of anhydrous HF on anhydrous $NiCl_2$, or nickel fluoride tetrahydrate at 300°C. It is also prepared by heating a mixture of NH_4HF_2 and $NiF_2{\cdot}4H_2O$. The other methods include the fluorination of metal salts using excess SF_4 (1) or using ClF_3 (2) at elevated temperatures, or the reaction of $NiCO_3$ and anhydrous HF at 250°C (3).

Nickel fluoride is used in marking ink compositions (see Inks), for fluorescent lamps (4) as a catalyst in transhalogenation of fluoroolefins (5), in the manufacture of varistors (6), as a catalyst for hydrofluorination (7), in the synthesis of XeF_6 (8), and in the preparation of high purity elemental fluorine for research (9) and for chemical lasers (qv) (10).

The 1993 price of high purity anhydrous nickel difluoride was $0.55/g in 100- or 250-g quantities. Small quantities are stored and shipped in polyethylene bottles, whereas large amounts are shipped in fiber board drums with polyethylene liners.

All nickel compounds are considered as suspected carcinogens and are listed in the EPA and TSCA's toxic substances inventory. LD_{50} (mice iv) for NiF_2 is 130 mg/kg (11–13).

2.1. Physical Properties

Anhydrous nickel fluoride has a mol wt of 96.71; mp, 1450°C; bp, 1740°C; solubility in water of 4.0 g/100 g; density, g/mL, of 4.72; ΔH_f of −651.5 kJ/mol (−135.3 kcal/mol); ΔG_f of −604.2 kJ/mol (−144.4 kcal/mol); S of 73.6 J/(mol·K) (17.6 cal/(mol·K)); and C_p, 75.3 J/(mol·K) (18.0 cal/(°C·mol)).

2.2. Other Nickel Fluorides

Nickel trifluoride has been observed during the electrolysis of the NiF_2·HF system as a brownish solid capable of liberating iodine from KI solution and turning into yellow powder (14). It has also been observed during the fluorination of NiF_2 at 200°C. A black substance obtained by the addition of AsF_5 to K_2NiF_6·HF solution and decomposing to NiF_2 during the purification process is also believed to be impure NiF_3 (15).

3. Nickel Fluoride Complexes

Nickel tetrafluoroborate [14708-14-6], $Ni(BF_4)_2{\cdot}xH_2O$, can be prepared by dissolving nickel carbonate in tetrafluoroboric acid [16872-11-0], HBF_4. Nickel tetrafluoroborate, commercially available as a hydrated solid, and also as a 50% solution, plays an important role in the electroplating (qv) and electronics industries. Its consumption is several hundred metric tons a year and its 1993 price was $4.25/kg. It is available from Advance Research Chemicals, Aldrich Chemicals, Aesar Chemicals, Johnson/Matthey, Harshaw M & T Chemicals, and from various other sources.

The complex hexafluoronickelates, M_2NiF_6 (M = Na [21958-95-2], K [17218-47-2], Rb [17218-48-3], Cs [17218-49-4]) and M_3NiF_6 (M = Na [22707-99-9], K [14881-07-3], Rb [72151-96-3], and Cs [72138-72-8]), are prepared by reaction of elemental fluorine, chlorine trifluoride, or xenon difluoride and a mixture of nickel fluoride and alkali metal fluorides or other metal halides (16, 17). If the fluorination is carried out using mixed fluorides, a lower temperature can be used, yields are quantitative, and the final products are of high purity. Bis(tetrafluoroammonium) hexafluoronickelate[63105-40-8], $(NF_4)_2NiF_6$, prepared from Cs_2NiF_6 and NF_4SbF_6 by a metathesis in anhydrous HF, is also known (18).

These hexafluoronickelates can be used as fluorinating reagents (15), as a source of high purity elemental fluorine (9, 10), and as high energy solid propellant oxidizers (see Explosives and propellants) (18).

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DAYAL T. MESHRI
Advance Research Chemicals, Inc.

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