Nitrogen trifluoride (NF$_3$): Production and purification

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1. Introduction

NF$_3$ is a toxic gas, inert under normal conditions, odorless in the absence of admixtures. At an elevated temperature it is a strong oxidizer comparable with fluorine.

General constants:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point, °C</td>
<td>-129 (1), -129.1 (2)</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>-206.8 (1), -208.5 (2)</td>
</tr>
<tr>
<td>Liquid density, g/cm$^3$</td>
<td>1.533 (1)</td>
</tr>
<tr>
<td>Evaporation heat, cal/mol</td>
<td>2769 (1)</td>
</tr>
<tr>
<td>Melting heat, cal/mol</td>
<td>95.1 (1)</td>
</tr>
</tbody>
</table>

Due to easy handling at room temperature, NF$_3$ has advantages compared with fluorine and is used as a stable fluorinating agent and has a wide application in high-energy chemical lasers, at dry etching in production of semiconductors, as a filling gas in lamps to prolong their durability and increase brightness, as a detergent gas in CVD apparatuses (chemical gas-phase precipitation) (3,4,77).

2. Methods of NF$_3$ production

For the first time, NF$_3$ was produced by O. Ruff et al. in 1928 by electrolysis of melt anhydrous NH$_4^+$ HF at 125°C, voltage of 7-9 V, current of 10 A in a copper electrolytic cell on a carbon anode (5).

This method was assumed as a basis for modern technologies to produce NF$_3$, the second industrial method is direct fluorination of ammonia.

Paper (6) presents a review based on publications right up to 1984 including data on methods of NF$_3$ production, purification, reactions with elements, organic and inorganic compounds and also its molecular properties, spectra, thermodynamic constants etc. That is why the present review considers only publications from 1983 y.

2.1. Electrolytic methods to produce NF$_3$

General data (6)

Electrolysis of NH$_4$F$^*(1,1-1,8)$HF melt is a main method to produce NF$_3$ on an industrial scale. Carbon materials and nickel are used as anode materials each of them has own merits and demerits. Carbon materials contrary to nickel are not liable to anodic dissolution, but during their use there are observed anode polarization (anodic effect), anodic corrosion and contamination of the goal product with carbon tetrafluoride. The process is described by the following equation:

$$\text{NH}_4\text{F}^*2\text{HF} \rightarrow \text{NF}_3 + 3\text{H}_2$$

or

$$2\text{NH}_4\text{F}^*\text{HF} \rightarrow \text{NF}_3 + \text{NH}_4\text{F} + 3\text{H}_2$$

(7)

When carbon-containing materials of the anode are used, N$_2$, N$_2$F$_2$, N$_2$F$_4$, NHF$_2$, nitrogen oxides, oxygen and CF$_4$ are formed together with NF$_3$ and H$_2$.

The optimal process parameters are as follows:

Temperature 100-120°C

Current density 0.12-0.15 A/cm$^2$

NF$_3$ current efficiency ~70%.

The electrolysis process is dangerously explosive due to the formation of a mixture of NF$_3$ with hydrogen and other components of electrolysis gas in the cell. To decrease the danger, the anodic and cathode spaces are separated with a diaphragm or the NF$_3$ concentration is kept beyond the bounds of explosiveness by nitrogen introduction into the cell.

Improvement of the electrolysis process

Within the period under review, a number of problems can be chosen which attracted intensive efforts of Japanese companies, particularly of Mitsui Chem. Inc.
1. Problems concerned with increasing safety of the electrolysis process owing to prevention of mixing anode and cathode gases.

This problem can be solved by the following measures:

**a) electrolytic cell modernization including**

- separation of anodic and cathode cells with fluoropolymer diaphragm (8)
- cell coating with a polymer resistant at temperatures above 140°C in places of contact with the melt and synthesis gases (9)
- certain location of the cell elements (electrodes, the diaphragm, the head):
  - the electrodes are placed below the diaphragm base (10)
  - the electrodes are placed at a distance of 30-200 mm from the separating diaphragm (11)
  - the electrodes, head and electrolyte surface are installed at a certain distance from each other (12,13)
  - two-level arrangement of the electrode cells preventing mixing anodic and cathode gases (14)

**b) a number of engineering approaches after the ending of NF$_3$ formation:**

- continuous or periodical arrangement of a potential between the anode and cathode (16)
- pressure control at gas-carrier supply into the anodic and cathode cells (15)
- purge with inert gas of the anodic cell equipped with a special nipple joints for gas output and input after the electrolysis stop till its activation (17)

Problems concerned with the formation of carbon tetrafluoride difficult to isolate from NF$_3$ and with the anodic effect in case of the use of carbon-containing materials for the anode. The following ways are used to solve these problems:

- keeping of the water concentration in the electrolyte within 0.01-1%, that is attained by water removal or addition of the starting material in amount of 0.1-10wt.% continuously or periodically (18). It is possible to decrease the water amount and prevent the anodic effect and also formation of CF$_4$ when the starting electrolyte is produced from dry gaseous NH$_3$ and HF (19):
  - to carry out the process at a current density above 50mA/cm$^2$ (20)
  - to use a high-strength anode:
    - with the resistance to bending of over 1000kg/cm$^2$ (21);
    - with the resistance to bending of over 50 MPA, current density of 4-30 mA/dm$^2$ and the ratio of HF/NF$_4$F in the electrolyte of 1-3 (22). The anode is made of porous carbon;
    - with the resistance to bending of over 50 MPA, current density of 50 mA/cm$^2$ max, potential between the cathode and neighboring anode of 6V max, quantity of electricity per 1 cm$^2$ of the anode surface of over 500 coulomb (23);
    - with the resistance to bending of over 50MPa, porous anode containing fluorides of Li, Na, Al, Mg, Ca, Ni. The process is carried out at a current density of 4-30 mA/dm$^2$ and a ratio of HF/NH$_4$F equal to 1-3 (24).
    - to carry out the process under control of pressure on the anode in dependence of which a necessary current density is provided. (25).

When metal anodes are used, their dissolution takes place with the formation of metal salts resulting in passivation of the anode and NF$_3$ yield decrease.

To increase the NF$_3$ yield it was proposed:

- to remove salts formed on the anode (26)
- to carry out forced convection of the electrolyte suppressing the formation of the salts (27)
- to use anodes made of special electrode composition produced by sintering Ni-containing oxides with coating of disperse nickel or nickel powder. The temperature of the process is 100-140°C, the ratio of NH$_4$F/HF in the electrolyte is 1-3 (28).

Increase in NF$_3$ purity produced during the electrolysis process.

- To increase the purity of NF$_3$, it is necessary to use the starting material of high purity produced from gaseous NF$_3$ of over 99.5 wt. % purity and HF of over 99.8 wt.% purity, nickel electrodes should have purity of 98.5 % min (29,30) or 99.5% min (31).

- The starting NH$_4$F contains 50 ppm of carbon maximum (32)
2.2. Investigation of possibility to produce NF3 using binary systems of electrolyte.

German researchers made attempts to produce NF3 in a higher yields using compounds with a higher valence as an additional nitrogen-containing component, for example hydrazine difluoride in NH4F*HF melt (33).

This attempt was not crowned with success since the following reactions take place on the anode in case of hydrazine use:

\[ 3N_2H_4 \rightarrow 4NH_3 + N_2 \]
\[ N_2H_4 \rightarrow N_2 + 4H^+ + 4e^- \]

Another direction of the investigation was possibility to use additives to NH4F*HF system with the purpose of simultaneous production of NF3 in a higher yield and a different process product. Sulfamoid fluoride H2NSO2F was taken as the additive (34,35).

H2NSO2F*NH4F*HF system behaved as a binary electrolyte and they failed to increase the current yield. Simultaneously it was possible to obtain NF3 from NH4+ and SO2F2 from H2NSO2F, at the same time increase in the H2NSO2F quantity resulted in an increase in SO2F2 yield but not NF3.

Similar behavior of NH4F*HF systems with additives of NH4N(SO2F)2 and (NH2)2SO2 was observed (36).

2.3. Doshisha University (Kyoto) investigations.

In the middle 80-s experts of Doshisha University continued a work started in the 60-s by N.Watanabe et al. devoted to the reactions taking place during electrolysis of salt melts with use of carbon-containing anodes and platinum reference electrodes. The purpose of the work was to determine the optimal conditions of NF3 formation.

Further study of electrolysis of KH2F2- RH2N systems, where CH3CONH2 and HCONH2 were used as RH2N, on an amorphous carbon electrode at 120°C has shown that the anodic effect was observed at a current density of 3-20mA/cm² and a film of carbon polyfluoride (CxF)n was formed on the anode. 1% LiF addition prevented the anodic effect but reduced the yield of NF3 and the water content in the melt. The maximum NF3 yield of 50.9% was obtained at a current density of 5.3 mA/cm² and 4 mol% of HCONH2 additive (37,38). The same yield under similar conditions was obtained when a glossy anode was used (39).

An addition of urea to a system of KH2F2 was studied earlier (40).

An addition of urea to a different system of NH4F-HF-KF gives the same results, i.e. an increase in the NF3 current efficiency due to removal of water which is consumed for urea hydrolysis and COF2 forming in the process. The maximum content of NF3 in the anode gas is 87% (41).

Later on investigations were carried out using NH4F*2HF melt and a nickel anode.

A possibility to improve the process parameters due to introduction of such additives as NH4NiF3, (NH4)3FeF6 and AlF3 to the electrolyte has been tested.

If the maximum NF3 yield attained 66% without additives at the anodic dissolution of 3%, then an addition of 0.1mol% of the most effective complex of NH4NiF3 reduced the anodic dissolution to 1%, but the NF3 yield reduced to 60% also (42,43,44). The process with the use of NH4NiF3 has been patented (45).

CsF (46,47) and LiF (48,49) were used as additives. The additives of these salts reduce the anodic dissolution and increase the NF3 yield. The processes using CsF and LiF have been patented (47,49).

Further studies on the effect of fluorides such as KF, MgF2, NaF, AIF3, CsF and LiF confirmed the effectiveness of CsF and LiF additives and showed that KF reduced the NF3 yield and stimulated the anodic dissolution (50,51).

A search for metal workable in NH4F*HF*CsF melt has found that Al, Fe, Mo, Nb, Sn, Ta and Ti are subjected to vigorous dissolution. Ag, Co, Cu, and Zn are also unusable because of passivation preventing from current passage.

Nickel was found the most acceptable metal for the anode, and also Monel, one of its alloys (52). Electrodes made of Ni-NiO1-x composite produced by HIP (hot isostatic pressing) method were also studied. The anode made of 10% composite was covered with a thick layer of oxides with infrequent porouness that prevented the anode from dissolution and increased the NF3 yield. An anode made of 20% composite has these parameters much worse. The anodes operated in NH4F*2HF melt (53).

An anode made of a different material, carbon impregnated with lithium fluoride, was studied in systems of NH4F-HF, KF-NH4F-HF, CsF-NH4F-HF. The yield of NF3 on these anodes is lower than that on nickel ones (53).
Further study of the anodic reactions on the nickel anode in melt of CsF-NH₄F*HF at 50-80°C allowed to conclude that an increasing the potential resulted in change of the anodic reactions and four zones were separated in dependence on the voltage:

- 0-1V (compared with H₂ standard electrode): nickel anodic dissolution
- 1-3V: deposition of Ni(II) compounds containing oxides (passivation)
- 3-5V: Ni(II) oxidation to Ni(III) and/or Ni(IV)
- over 5V: proper NF₃ purification

The anode gas is composed of NF₃ and N₂ with a small additive of O₂, N₂O, N₂F₂, N₂F₄ (55). A similar picture is observed in melts of (CH₃)₄NF₆*HF and (CH₃)₄NF₆*HF + 50% CsF*2HF, where m=3.5+0.5n (n=1-4).

Here also 4 zones are seen. An oxidized layer is formed at a potential above 4V and is composed of NiF₂, fluorides with high oxidation level and a small quantity of oxides of different valence (56). Paper (57) describes a mechanism of fluoride films formation on the anode. This phenomena and possible effect of fluoride layers on the fluorination process have been reviewed in paper (54).

3. Ammonia direct fluorination

Ammonia fluorination in NH₄F*HF melt is far more practically feasible process than gas-phase fluorination. That allowed Air Products and Chem. to implement this process on an industrial scale and produce the product of 99.5% purity (6).

Later on research in this field was directed to

1. expansion of a source of raw materials
   - (NH₄)₂AlF₆, (NH₄)₂SiF₆ and (NH₄)₂NaAlF₆ were proposed as a starting solid complex. Their interaction with fluorine is conducted at a temperature below 150°C. The product obtained has a purity of 98.5% (58)
   - metal fluorides in a mixture with ammonium salt at fluorination with elemental fluorine diluted with nitrogen give NF₃ in 96.9% yield (59)

2. search of solutions on prevention of clogging apparatus
   - to produce NF₃ by gas phase method at a ratio of F₂/NH₃ equal to 3-20, it is envisaged to place a reactor in a heating area at 80-250°C (60)
   - two plates are placed in the reactor with a gap of 0.1-10cm (61)
   - fluorine and ammonia used in the gas phase process are charged through a spiral along the inside reactor wall for mixing and interaction. The formation of NH₄F₂ resulting in clogging is prevented (62).

A processing line with circulation of a melt containing ammonia, metal fluoride and HF has been patented. The processing line includes the following equipment through which the melt circulates: an electrolyzer to produce fluorine and hydrogen, a reactor for NF₃ production and 2 apparatuses- solubilizers located between them, one apparatus at the output of the melt from the electrolyzer and the second one at the input. Gas-carrier together with ammonia and fluorine respectively are charged into these apparatuses to keep the ammonia and HF concentration constant in the melt. Fluorine mixed with the gas-carrier comes to the reactor where it reacts with the melt to form NF₃ (63).

Paper (64) suggests to carry out interaction of elemental fluorine with ammonia complex NH₄F*HF, (NH₄)₁₋₄MF₂₋₈*nHF (where M is an element of I A-V A group, I B-VII B group and VIII group) at mixing of the melt complex with a turbine-type mixer.

4. NF₃ purification methods

Modern electronic industry makes high demands for NF₃ purity right up to 99.999% in which connection a great attention is paid to NF₃ purification.

Methods for NF₃ treatment for removal of acid and hydrolyzable admixtures and difluorodiazine, N₂F₂, have been described in (6). N₂F₂ was removed by decomposition over a nickel-containing catalyst at 240°C, for example in a nickel pipe filled with nickel balls or other nickel packing. In this case the content of N₂F₂ is reduced from over 0.1% to less than 0.01%.

NF₃ catalytic purification from N₂F₂ with nickel-containing compounds was further developed in the work of Mitsui Toatsu Chem. Inc. They used heating NF₃ raw at 150-600°C in a vessel covered with nickel fluorides. The vessel coating was made by its treatment with fluorine (66, 67, 68, 69, 70, 71). To increase the purification level, the vessel may be filled with fluorides (69-72), for example with fluorides of nickel or calcium (74).

To purify NF₃ from N₂F₂ and/or OF₂ it is suggested to use other fluorides:

- tablets made from NaF melt and polyvinyl alcohol preheated at 850°C before use (75)
Sorbents are widely used for NF₃ purification. A process with their use is carried out in adsorption or chromatographic regime.

- when NF₃ containing 1.7% of N₂F₂ is contacted silica gel, the content of N₂F₂ is reduced to 20 ppm (76)
- silica gel preheated and preliminarily dried at a temperature of 150-300°C effectively removes N₂O and CO₂ at a temperature of 125°C (68, 70, 77)
- anhydrous aluminum oxide (Al₂O₃) at 250-900°C and the same adsorption temperature removes N₂O and CO₂ (69, 71, 79)
- activated carbon after preliminary removal of acid admixtures from NF₃ purifies it completely from N₂F₂ and N₂F₄ (78, 83)
- SiO₂ with interstices of 3-10 mm is applied for removal of nitrogen oxides without NF₃ losses (80)

Purification with use of natural and synthetic zeolites (81) is also wide spread.

Before use, zeolites are preheated in a nitrogen flow at a temperature of 270-700°C (81, 85, 86). For their reuse, the heating is conducted step-by-step, first at 50-200°C, then at 250-700°C (87, 88). To ensure the uniform heating of zeolites, metal perfluorinated disc-shaped plates are inserted in the zeolites (89). A purification temperature with use of zeolites is 125-110°C.

The following admixtures are removed by means of zeolites:

- N₂O and N₂F₂, in this case it is recommended to carry out additional treatment of zeolites with solutions of sodium salts of organic and inorganic acids with subsequent heating at 250-700°C (82)
- N₂O and CO₂ (90, 91, 92, 93, 86)
- water for which removal natural (93) and synthetic (94) zeolites of 3A type are used

To separate NF₃ and CF₄ a chromatography method is applied using zeolites of 3A type either containing 1-10% of water (84) or preliminarily wetted with water and heated for 16 hours at 300°C in inert medium of chabazite or zeolite of 5A type with the pore surface of 4.4-4.8 Å. The charge of the flow to be separated is executed in a pulse regime. Purification of the separated gases reaches 99.99% (95).

SiO₂ adsorbents, carbon molecular sieves, Al₂O₃, macro-cross-linked polymers, kieselgur, active carbon, aluminosilicates and zeolites containing also chemosorbents for decomposition of admixtures may be used for sorption storage of gases in a special adsorption-desorption apparatus. A gas to be desorbed is charged directly to a CVD apparatus or a laser plant (107-109).

Low-temperature rectification in the presence of a third component (He, Ar, Ne etc.) is used for purification of NF₃ from N₂F₂, CO₂, O₂, N₂ (96-98). A complex of procedures for NF₃ purification including sorption purification and rectification in columns of middle and low pressure has been patented (99).

A method to purify NF₃ from CF₄ by azeotropic and extractive low-temperature rectification to the content of admixtures of 10 ppm was described in (111).

The following methods of NF₃ purification were also described:

- to purify from HF and OF₂, the raw gas is first washed with water or a solution of NaOH, then it is treated in a scrubber with aqueous solution of Na₂S₂O₃, HI or Na₂S (100)
- application of a reactive micromatrix containing organo-metalic compounds allows to reduce admixtures to ppb level and even lower (101)
- to remove water from a number of gases including NF₃, a process including distillation of water and its separation from the gases was patented (102)
- to remove N₂F₂, purification by UV radiation treatment with subsequent contacting the gas with adsorbents was suggested (103)
- processes of NF₃ separation from a gas-diluent by means of selective membranes are described in (104, 105)

Usually the purified NF₃ is stored in cryogenic tanks (91, 92) including tanks joined to a heat exchanger for NF₃ condensation (106).

Gases containing NF₃ and admixtures are fractionated by gas chromatography method and analyzed by IR-spectroscopy (46), gas chromatography identification of NF₃ traces is also known (110).

The water content in NF₃ less 50 ppm may be determined by laser spectroscopy (112).

**References**