

Short Communication

The possibility of separating hydrogen fluoride from its gaseous mixture with silicon tetrafluoride

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We report in this paper investigations of the conditions necessary to effect the selective absorption of hydrogen fluoride from its gaseous mixture with silicon tetrafluoride when that mixture is brought into contact with solid sodium fluoride. Thus, when an anhydrous HF-SiF₄ gas mixture is brought into contact with granular NaF at room temperature only hydrogen fluoride is absorbed (giving NaF•HF), while silicon tetrafluoride remains in the gaseous state. In this way it is possible to separate HF from SiF₄. The hydrogen fluoride may subsequently be regenerated by heating the sodium hydrogen fluoride at 350–400°¹. If, however, the gaseous mixture contains only small traces of water vapor then SiF₄ also reacts with NaF to give Na₂SiF₆ in addition to NaF•HF. Under these circumstances it is not possible to effect a separation.

Experimental

All experiments were conducted by passing a stream of gaseous HF and SiF₄ (mole ratio HF:SiF₄ = 2:1) through a column containing granular NaF at room temperature. The gaseous mixture of HF and SiF₄ was generated by treating anhydrous sodium fluosilicate with concentrated sulfuric acid in a reactor. A slow stream of air was passing through the reactor to accelerate the evolution of HF and SiF₄.

Results and discussion

The following results were obtained:

- (i) When the stream of air passed through the reactor had not been previously dried (40–70 % relative humidity), up to 70–73 % of the fluorine content of the resulting granular product in the column was present as Na₂SiF₆. The remaining fluorine was present as NaF•HF or unchanged NaF. Hence when water vapour is present in the system the resulting absorption of HF upon NaF is not selective.
- (ii) Thoroughly drying the stream of air before its passage through the system resulted in the granular product in the column containing no silicon and consisting entirely of NaF•HF and NaF. Under these conditions absorption of HF upon

NaF occurs selectively and quantitatively and the separation of HF from SiF₄ may be effected.

The presence of Na₂SiF₆ as an absorption product in addition to NaF•HF when non-anhydrous conditions are maintained in the system at room temperature may be explained as follows. In the absence of water NaF and SiF₄ react only at elevated temperatures², probably due to the relatively high activation energy necessary to effect the transition from the cubic crystal lattice characteristic of NaF³ to the hexagonal lattice of Na₂SiF₆. When SiF₄ and NaF are brought into contact at room temperature in the absence of water, this activation energy is not available and the formation of Na₂SiF₆ does not occur. If only traces of water are present in the system, however, the ease with which transformation of the NaF crystal lattice is effected is considerably enhanced possibly by association between the Na⁺ and F⁻ ions in the crystal lattice and H₂O molecules via the dipoles present in the latter or alternatively through coordination between H₂O molecules and the silicon in the SiF₄ molecule, thus stimulating the transition from the tetrahedral arrangement characteristic of fluorine atoms in the SiF₄ molecule to the octahedral arrangement existing in the SiF₆²⁻ ion⁴. This leads to a lower activation energy for the conversion of NaF into Na₂SiF₆, so that in this context water is probably acting as a catalyst.

REFERENCES

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