

## IDENTIFICATION OF H<sub>2</sub>SiF<sub>6</sub>, and definition of Boundary composition

### 1- FOREWORD

Hexafluorosilicic Acid has been identified with EC no. 241-034-8, CAS no. 16961-83-4 according to the EINECS inventory, and registered as a mono- constituent substance.

However, Hexafluorosilicic acid doesn't exist in its anhydrous form, only in the presence of water in aqueous solutions, where there is no molecular form of fluorosilicic acid but several equilibria between SiF<sub>4</sub>-H<sub>2</sub>O-HF-SiF<sub>6</sub><sup>2-</sup>-SiO<sub>2</sub>, as mentioned by the available bibliography.

H<sub>2</sub>SiF<sub>6</sub>, does not exist as an independent substance and consequently when referring to Hexafluorosilicic acid it is more appropriate and expedient to refer to a system" characterized in terms of specific quantities of HF, H<sub>2</sub>SiF<sub>6</sub>, SiO<sub>2</sub> and H<sub>2</sub>O.

Since Hexafluorosilicic acid doesn't exist in anhydrous form it makes no sense to attempt to express concentration of other impurities referred to 100% simply because it is not real. Impurities will be always belonging to the substance in presence of water. The upper concentration level of Hexafluorosilicic acid manufactured and available on the market is 47%. Meanwhile substance stability limit found in the literature is around 60% concentration of H<sub>2</sub>SiF<sub>6</sub> in water.

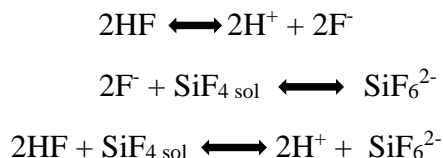
### 2- CHEMISTRY OF HEXAFLUOROSILICIC ACID

In the scientific literature <sup>(1)</sup> evidence is found that on passage of SiF<sub>4</sub> into concentrated HF acid, crystals of H<sub>2</sub>SiF<sub>6</sub>·2H<sub>2</sub>O are formed. This solution deliquesces easily, fumes in air, and melts at appr. 19°C. In attempts to isolate dihydrates during the absorption of silicon tetrafluoride by concentrated HF acid at a temperature below 0°C (2-3 moles of water per mole of HF), crystals are obtained, d=1.7, which fume in air and decomposes slowly, and melts somewhat above 0°C, into syrupy liquid. This composition was described with formula H<sub>2</sub>SiF<sub>6</sub>·4H<sub>2</sub>O. Even more, if more concentrated HF acid (2 moles HF per 1 mole water) is used, then at a temperature below -2°C crystals of H<sub>2</sub>SiF<sub>6</sub>·4H<sub>2</sub>O are formed, which fumes strongly in air and melts around -20°C.

According to research a 30.20% solution of H<sub>2</sub>SiF<sub>6</sub> can be supercooled to -50°C, and a frozen solution melts at -35°C. The crystals separated from the mother liquor melt at -13°C and are evidently a crystal hydrate of Fluorosilicic acid. Hydration of the cations strengthen the complex anion. The possibility of forming anhydrous acid is not excluded, however, the crystal hydrate H<sub>2</sub>SiF<sub>6</sub>·H<sub>2</sub>O is actually a crystal hydrate of silicon tetrafluoride.

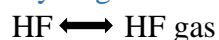
**Furthermore, the molecule H<sub>2</sub>SiF<sub>6</sub> does not exist as such in aqueous solution since in contact with water it is dissociated into several species in equilibrium with each other (see below).**

It follows that the high hydrogen ion concentration in the solutions is to be explained not by the electrolytic dissociation of Fluorosilicic acid c. a. 60% aqua solution, EC 241-034-8, CAS 16961-83-4 (CLP Annex VI, note B substance), but by an abrupt displacement to the right in the position of the electrolytic dissociation equilibrium of HF, caused by the binding of fluoride ions into the comparatively stable complex ion SiF<sub>6</sub><sup>2-</sup>:

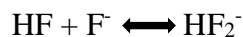
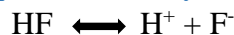


Raising the  $\text{H}^+$  concentration by the introduction of strong acid lowers the stability of the complex ion and displaces the position of the overall equilibrium to the left. The properties of the  $\text{H}_2\text{SiF}_6$  solution can be completely understood by following the independent equilibriums:

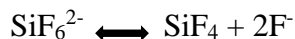
#### 2.1 The vaporization equilibrium of hydrogen fluoride and silicon tetrafluoride:



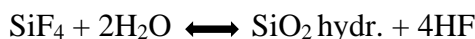
#### 2.2 The electrolytic dissociation equilibrium of hydrofluoric acid



#### 2.3 The dissociation equilibrium of $\text{SiF}_6^{2-}$ into dissolved silicon tetrafluoride and $\text{F}^-$ ions



#### 2.4 The hydrolysis equilibrium of dissolved silicon tetrafluoride:



In the case of the existence of silicon fluorohydroxy-complexes, for example  $[\text{SiF}_5\text{OH}]^{2-}$  or  $[\text{SiF}_4(\text{OH})_2]^{2-}$  the scheme of equilibriums shown above would have to be correspondingly complicated. **However, experimental data known at the present time do not indicate the existence of ions of this sort.**

The equilibrium conditions of process 2.4 depend substantially on the thermodynamic properties of silicic acid and on whether the solution is saturated with the acid. It is obvious that in an unsaturated silicic acid solution the HF activity is increased and  $\text{SiF}_4$  activity is decreased. In the same way the precipitation of silicic acid in solutions saturated by it also causes decrease in activity.

### 3- IDENTIFICATION OF HEXAFLUOROSILICIC ACID

**Based on the information that "dry"  $\text{H}_2\text{SiF}_6$  is not stable as a substance, a 100 % pure ("dry")  $\text{H}_2\text{SiF}_6$  IS NOT an appropriate description of the substance.** Consideration of water would further reduce the concentration of the impurity HF since the HF concentration would not be based on  $\text{H}_2\text{SiF}_6$  but on the aqueous solution of  $\text{H}_2\text{SiF}_6$  within the maximum range of substance's stability. In fact, a substance is defined by REACH (Article 3(1)) and in CLP (Article 2(7)) as following:

*"Substance means a chemical element and its compounds in the natural state or obtained by any manufacturing process, including any additive necessary to preserve its stability*

*and any impurity deriving from the process used, but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition.”*

**Based on all independent equilibria described above under point 2, the solvent water cannot be excluded above the threshold at which the stability of fluorosilicic acid is affected.**

**Based on literature data, the concentration threshold of stability of H<sub>2</sub>SiF<sub>6</sub> is 60.70 %, corresponding to a density at 25<sup>0</sup>C of 1.4634 g/cm<sup>3</sup>.**

#### 4- DETERMINATION OF HF IMPURITY

Hexafluorosilicic acid is manufactured as a concentrated solution that contains excess of F in relation to the Si expected from the theoretical (**stoichiometric**) values. **The way of analyzing H<sub>2</sub>SiF<sub>6</sub> is the EN standard 12175 in which equilibria are displaced in order to express the composition as H<sub>2</sub>SiF<sub>6</sub> and the excess of fluorides expressed as HF, but it doesn't mean "free HF" exists as itself.** It is only a way of expressing the results obtained in the analytical method which is not specific for determining HF.

- The presence of free HF shall be based on stoichiometric calculations and supported by NMR analysis.

**According to relevant reports from NMR tests carried out on H<sub>2</sub>SiF<sub>6</sub>**

*“The 1H-NMR spectrum shows the expected signals for: "Fluorosilicic Acid". A small signal of an unknown side component is visible.*

*The 1H-, <sup>19</sup>F- and <sup>29</sup>Si-NMR spectra of the test item show the expected signals for the given structure (dissolved Hexafluorosilicic acid). The <sup>1</sup>H- and <sup>19</sup>F-NMR spectra show signals of unknown side components.”*

*“Referring to our report xxxxxxxx on the characterization of aqueous hexafluorosilicic acid, we have discussed the unknown side component, which appeared mainly in the <sup>19</sup>F-NMR spectrum at  $\delta_F \sim -xx$  ppm. Likewise, the <sup>1</sup>H-NMR spectrum showed an extremely small signal for a side component ( $\delta_H \sim +0.39$  ppm) which, however, is only visible after zooming the spectrum in the corresponding spectral region. We consider this minor <sup>1</sup>H-NMR signal as irrelevant with respect to registration purposes.*

*Regarding the <sup>19</sup>F-NMR data, we have calculated the integral of the signals of the unknown species at  $\delta_F \sim -149.9$  ppm in relationship to that of the main component [SiF<sub>6</sub>]<sup>2-</sup> (at  $\delta_F \sim -xx$  ppm) in order to estimate their relative quantities. This calculation revealed that on the basis of the fluorine content the minor, unknown species only accounts for approx. 0,xxx mol-% with respect to the main component”*

**“...from our chemical knowledge, the presence of at least a small quantity of species other than [SiF<sub>6</sub>]<sup>2-</sup> should be expected in aqueous solutions of H<sub>2</sub>SiF<sub>6</sub> due to interaction of the predominant species [SiF<sub>6</sub>]<sup>2-</sup> and water, which may lead to some degree of hydrolysis (equilibria). Hence, we assume the additional <sup>19</sup>F-NMR signal at  $\delta_F \sim -xx$  ppm is most likely to be related to the main component and not to an “external” impurity of other origin in your particular sample.**

*Our literature search yielded a very recent PhD thesis (2) which addresses a range of equilibria involving H<sub>2</sub>SiF<sub>6</sub>. This thesis also contains a short chapter on spectral data (including <sup>19</sup>F-NMR) of various fluorosilicon-based species.”*

According to bibliography the final assumption that the unknown component is SiF<sub>4</sub> coordinated with water, or SiF<sub>5</sub><sup>-</sup> or similar compounds but it is not conclusive on detecting "free HF".

## 5- CONCLUSIONS AND DEFINITION OF BOUNDARY COMPOSITION

5.1 Hydrofluoric acid (HF) is not expected to be available as such (in its "free" form), unless a presence exceeding stoichiometric ratio is triggered by company specificities ; the presence of free HF **shall be based on stoichiometric calculations** and supported by NMR findings (because of different free HF results got from the standard EN12715). In our opinion based on H<sub>2</sub>SiF<sub>6</sub> chemistry above described, we believe that EN12715 standard methods gives higher results on "free HF" in comparison with a specific technique for HF because of equilibrium displacement caused by this analytical method.

5.2 Water has to be considered as part of the substance because below a certain solvent concentration the substance stability is affected. Thus, the minimum amount of water that cannot be removed without affecting the stability of H<sub>2</sub>SiF<sub>6</sub> has to be considered as additive and included in the substance composition reported in the dossier.

The additive is not a constituent, and the impurities either taken singularly and altogether do not exceed the concentrations limits given in the ECHA guidance for identification and naming of substances for a mono-constituent substance, hence the substance is identified as a mono-constituent, which boundary compositions are given as following :

### 5.2.1 Boundary composition 0-0.25 HF

#### **Name: Hexafluorosilicic acid**

Type of composition: Boundary composition

State / form: liquid

Degree of purity:  $\geq 91.75\%$  -  $\leq 100\%$  (w/w)

**Constituents: Hexafluorosilicic acid (EC 241-034-8, CAS 16961-83-4)**

Typical concentration:  $\geq 55.69\%$  (w/w)

Concentration range  $\geq 55.69$  —  $\leq 60.7\%$  (w/w)

#### **Impurities:**

Hydrogen Fluoride (EC 231-634-8, CAS 7664-39-3)

Typical concentration:  $< 0.25\%$  (w/w)

Concentration range:  $\geq 0\%$  -  $\leq 0.25\%$  (w/w)

Other inorganic not influencing classification:  $\geq 0\%$  -  $\leq 8\%$  (w/w)

#### **Additive:**

Stabilizer (Other) Water (EC 231-791-2, CAS 7732-18-5)

Typical concentration:  $\geq 36.06\%$  (w/w)

Concentration range:  $\geq 36.06\%$  -  $\leq 39.30\%$

### 5.2.2 Boundary composition 0.25-0.5 HF

**Name: Hexafluorosilicic acid**

Type of composition: Boundary composition

State / form: liquid

Degree of purity:  $\geq 91.5\%$  -  $\leq 99.75\%$  (w/w)

**Constituents: Hexafluorosilicic acid (EC 241-034-8, CAS 16961-83-4)**

Typical concentration:  $\geq 55.54\%$  (w/w)

Concentration range  $\geq 55.54\%$  —  $\leq 60.7\%$  (w/w)

**Impurities:**

Hydrogen Fluoride (EC 231-634-8, CAS 7664-39-3)

Typical concentration:  $< 0.50\%$  (w/w)

Concentration range:  $\geq 0.25\%$  -  $\leq 0.50\%$  (w/w)

Other inorganic not influencing classification:  $\geq 0\%$  -  $\leq 8\%$  (w/w)

**Additive:**

Stabilizer (Other) Water (EC 231-791-2, CAS 7732-18-5)

Typical concentration:  $\geq 35.96\%$  (w/w)

Concentration range:  $\geq 35.96\%$  -  $\leq 39.3\%$

### 5.2.3 Boundary composition 0.5-1.0 HF

**Name: Hexafluorosilicic acid**

Type of composition: Boundary composition

State / form: liquid

Degree of purity:  $\geq 91.0\%$  -  $\leq 99.50\%$  (w/w)

**Constituents: Hexafluorosilicic acid (EC 241-034-8, CAS 16961-83-4)**

Typical concentration:  $\geq 55.24\%$  (w/w)

Concentration range  $\geq 55.24\%$  -  $\leq 60.7\%$  (w/w)

**Impurities:**

Hydrogen Fluoride (EC 231-634-8, CAS 7664-39-3)

Typical concentration:  $< 1.00\%$  (w/w)

Concentration range:  $\geq 0.5\%$  -  $\leq 1.0\%$  (w/w)

Other inorganic not influencing classification:  $\geq 0\%$  -  $\leq 8\%$  (w/w)

**Additive:**

Stabilizer (Other) Water (EC 231-791-2, CAS 7732-18-5)

Typical concentration:  $\geq 35.76\%$  (w/w)

Concentration range:  $\geq 35.76\%$  -  $\leq 39.30\%$

### 5.2.4 Boundary composition 0.5-1.6 HF

**Name: Hexafluorosilicic acid**

Type of composition: Boundary composition

State / form: liquid

Degree of purity:  $\geq 90.4\%$  -  $\leq 99.50\%$  (w/w)

**Constituents: Hexafluorosilicic acid (EC 241-034-8, CAS 16961-83-4)**

Typical concentration:  $\geq 54.87$  % (w/w)

Concentration range  $\geq 54.87$  -  $\leq 60.7$  % (w/w)

**Impurities:**

Hydrogen Fluoride (EC 231-634-8, CAS 7664-39-3)

Typical concentration:  $< 1.6$  % (w/w)

Concentration range:  $\geq 0.5\%$  -  $\leq 1.6$  % (w/w)

Other inorganic not influencing classification:  $\geq 0\%$  -  $\leq 8$  % (w/w)

**Additive:**

Stabilizer (Other) Water (EC 231-791-2, CAS 7732-18-5)

Typical concentration:  $\geq 35.53$  % (w/w)

Concentration range:  $\geq 35.53\%$  -  $\leq 39.30\%$

**NOTE:** The anhydrous form is required for registration purposes. However, hexafluorosilicic acid in anhydrous form does not exist in nature and exists only stabilized by water as an aqueous solution. Furthermore, hexafluorosilicic acid water solutions are manufactured/imported and placed in the market exclusively in concentrations lower than 47%. The boundary composition of hexafluorosilicic acid includes the minimum amount of water necessary to preserve the stability of the substance. Water in excess to the boundary composition, that is always present in the substance placed in the market, is not regarded necessary to preserve the stability of the substance, but is to be regarded only as a solvent (or diluent) and has not to be indicated as belonging to the substance composition.

However, the full amount of water has to be taken in account when the concentration of the substance in water solution is calculated.

The above approach is consistent with Regulation EC/1272/2008, where in the Annex VI the substance is listed as “fluorosilicic acid...%” EC241-034-8 CAS 16961-83-4, (note B), and where no entries are given for “Hexafluorosilicic acid”.

*Note B: Some substances (acids, bases, etc.) are placed on the market in aqueous solutions at various concentrations and, therefore, these solutions require different classification and labeling, since the hazard varies at different concentrations. In Part 3 entries with Note B have a general designation of the following type “nitric acid...%”*

**Literature references:**

- (1) The chemistry of Fluorine and its inorganic compounds I. G. Ryss,
- (2) Untersuchungen zur Abtrennung von Hexafluorosilicat aus Ätzbädern C. Rissom – Dissertation 2013)