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A.F. Holleman, The preparation of silicon and its chloride, in:
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investigation, and of which the theory of VAN DER WAALS could give a closer description.

The peculiarity of the examined system, which lies in the fact that the vapour pressure of the one substance (ether) far exceeds that of the other (anthraquinone), caused some wholly unexpected phenomena, and made it on the other hand possible to realize retrograde solidification on a much larger scale than had been thought possible till now.

Laboratory for Anorganic Chemistry of the University.

Amsterdam, June 1904.

Chemistry. — “*The preparation of silicon and its chloride.*” By Prof. A. F. HOLLEMAN.

(Communicated in the meeting of June 24, 1904).

The numerous proposals which have been made for the preparation of the element silicon in both the amorphous and crystallised form prove that a simple method has not as yet been found. W. HEMPEL and von HAASY¹⁾ have published in 1899 an additional process consisting in the decomposition of silicon fluoride with sodium. They melt this metal in small portions at a time in an iron apparatus and then pass over the mass a current of silicon fluoride, which is then very readily decomposed. The brown porous mass, which has been brought to a faint red heat is allowed to cool for two or three hours in the current of silicon fluoride. An attempt to convert it into silicon chloride by heating the mass without previous purification in a current of chlorine was unsuccessful. It was impossible to remove the Na Fl and Na₂Si Fl₆ by boiling with water; so in order to obtain pure silicon it was necessary to fuse the mass with sodium and aluminium. The latter dissolves the silicon which is then left insoluble on treating the regulus with dilute hydrochloric acid.

Mr. H. J. SLIJPER who has repeated these experiments in my laboratory showed (1) that by a small modification of the process the crude product may be purified to such an extent by boiling with water that it may be used for preparing silicon chloride; (2) the reason why the crude product on being treated with chlorine does not yield silicon chloride.

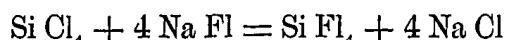
1. It is known that sodium fluoride readily absorbs Si Fl₄ and

¹⁾ Zeitschr. f. anorg. Ch. 23, 32.

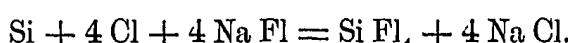
passes into Na_2SiFl_6 . By allowing their apparatus to cool for 2 to 3 hours whilst transmitting this gas HEMPEL and von HAASY practically converted the sodium fluoride, which had been formed according to the equation: $4\text{Na} + \text{SiFl}_4 = 4\text{NaFl} + \text{Si}$, into sodium fluosilicate, which is soluble in water with great difficulty. If, however the action of SiFl_4 is stopped as soon as all the sodium has been introduced into the apparatus, it is easy to almost completely avoid the formation of Na_2SiFl_6 . 100 grams of sodium yielded to Mr. SLIJPER 219 grams of crude material ($4\text{NaFl} + \text{Si}$) instead of 213.6 the quantity calculated; 55 grams of the Na gave 119 grams, theory 117.2, and in some further experiments the theoretical quantity was but little exceeded. By washing and boiling with water and with dilute hydrochloric acid the 119 grams were reduced to 20 grams whilst the product may contain 16.7 grams of silicon. The product so obtained is not, however, pure amorphous silicon, only about 40 per cent is volatilised in a current of chlorine and may be condensed as silicon chloride, and a residue is obtained, which is only to a slight extent soluble in water and principally consists of silicon dioxide.

This must have been formed during the washing; for if the crude product is heated in a current of chlorine there remains besides sodium chloride only a very small quantity of insoluble residue. As the crude product when immersed in water causes a visible evolution of gas with the odour of SiH_4 it is probable that the SiO_2 has been formed by decomposition of SiH_4 which may have been produced by the action of water on some sodium silicide. MOISSAN has recently shown that on treating silicon with boiling water the dioxide of that element is formed.

2. In accordance with HEMPEL and von HAASY, Mr. SLIJPER found that on heating the crude product in a current of chlorine not a trace of silicon chloride is obtained. As the said product consists mainly of $4\text{NaFl} + \text{Si}$, it was surmised that this must be attributed to the fact that the primary formed silicon chloride reacts with sodium fluoride according to the equation



It appeared indeed that on heating sodium fluoride or sodium fluosilicate in the vapour of silicon chloride the said decomposition takes place. If, therefore, chlorine is passed over a mixture of Si and NaFl as is present in the crude product the reaction must proceed in this manner:



That such is practically the case was shown by the fact that the gas evolved consisted of SiF_4 , and that the substance left behind in the boat was found to be almost pure sodium chloride.

A better method of preparing amorphous silicon seemed to be the decomposition of silicon chloride by sodium. When boiled in benzene-solution with sodium or potassium no action took place. A reaction, however, took place on heating sodium in the vapour of silicon chloride, but it became very violent; the brown powder obtained could certainly be readily freed from sodium chloride by means of water, but on heating in a current of chlorine a large amount of SiO_2 (about 30 %) was left behind showing that even this process does not lead to pure amorphous silicon.

Much more simple is the preparation of *crystallised* silicon according to the method recently published by R. A. KÜHNE (Chem. Centr. 1904, I. 64) if we introduce a slight modification. A mixture of 200 grams of aluminium shavings or powder, 250 grams of sulphur and 180 grams of fine sand is put into a Hessian crucible placed in a bucket with sand. Upon the mixture is sprinkled a thin layer of magnesium powder and this is ignited by means of a GOLDSCHMIDT cartridge. The mass burns with a beautiful light and the contents of the crucible become white hot. When cold, the mass is treated with dilute hydrochloric acid, which dissolves the aluminium sulphide and leaves the silicon in a beautifully crystallised state. The yield amounts to about 30 grams. On heating in a current of chlorine SiCl_4 is very readily formed, only 3% remaining as non-volatile products. It is a material eminently suited for the preparation of SiCl_4 , but Mr. SLIJPER did not succeed in converting it into silicon sulphide by heating with sulphur.

Groningen, Lab. Univers. March 1904.

Crystallography. — “*On the preservation of the crystallographical symmetry in the substitution of position isomeric derivatives of the benzene series*”. By Dr. F. M. JAEGER. (Communicated by Prof. A. P. N. FRANCHIMONT).

(Communicated in the meeting of June 24, 1904).

Some time ago when engaged in a research as to the connection between molecular and crystallographical symmetry of position-isomeric benzene derivatives¹), I demonstrated, that of the six possible *tribromo-*

¹⁾ JAEGER, Crystallographic and Molecular Symmetry of position-isomeric Benzene-derivatives. Dissertation, Leiden 1903. (Dutch).