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A REVISION OF THE ATOMIC WEIGHT OF SILICON. THE ANALYSIS OF SILICON TETRACHLORIDE.

Preliminary Paper.

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Present knowledge of the atomic weight of silicon is in a far from satisfactory state. Even the more modern determinations of this constant vary from 28.0 to 28.4. In his "Recalculation of the Atomic Weights," Clark,[1] from a consideration of all available data, finds the value 28.25 and the value 28.3 has been adopted by the International Committee on Atomic Weights. The atomic weight of silicon is a particularly important one from a geological and mineralogical point of view, since silicates constitute so large a proportion of the earth's crust. Because of this importance, and because our preliminary experiments indicate a value quite different from the value in common use we have thought it desirable to present the results of these experiments without waiting for the completion of the research.

We chose the method which has already been used by Dumas[2] of comparing silicon tetrachloride with silver; for the tetrachloride is readily purified by distillation, and the comparison of a chloride with silver is one of the most accurate of analytical processes. These advantages outweigh the disadvantage of the small percentage of silicon in the tetrachloride, 16.5.

Preparation of Silicon Tetrachloride.[3]

One portion of the silicon tetrachloride was made by passing dry chlorine from a cylinder over hot powdered silicon and condensing the product in a flask cooled with ice. The product contained a red precipitate, presumably ferric chloride, which was easily removed by filtration through glass wool. This material, which contained an excess of chlorine, was mixed with a portion obtained from the General Electric Company, and the mixture was admitted, together with several cc. of mercury, through a separatory funnel into an exhausted flask, and the separatory funnel was sealed off. In order to eliminate the excess of chlorine, the chloride was left in contact with the mercury for a week in the exhausted flask.

The impurities chiefly to be feared in this material were decomposition products resulting from hydrolysis, *i. e.*, silicic acid and hydrochloric

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[1] *Smithsonian Inst. Pub.*, "Constants of Nature," Part V, p. 278 (1910).

[2] *Ann. chem. pharm.*, 113, 31 (1860). Schiel also determined the chlorine in silicon tetrachloride as silver chloride, *ibid.*, 120, 94 (1861).

[3] The preparation and distillation of silicon tetrachloride were carried out by Mr. Holmes.

acid, besides silicon hexachloride, carbon tetrachloride and titanium tetrachloride. Since the boiling point of silicon tetrachloride is 58° and those of the last 3 substances are 144–8°, 76.5° and 136°, respectively, it seemed reasonable to hope that the silicon tetrachloride could be effectively purified by fractional distillation. Such a process was carried out at low temperatures by condensing the chloride at the desired point by means of either liquid air or a carbon dioxide-alcohol mixture.

The exhausted flask, to which was attached a special valve such as was used by Briscoe[1] and later by Baxter and Starkweather,[2] was sealed to a system of 3 small bulbs and a flask to which also a special joint had been attached. After this system had been evacuated, the special joint attached to the first flask was opened by breaking the capillary, and then the 3 bulbs and finally the flask were successively filled with silicon tetrachloride by chilling, each bulb being sealed off as soon as nearly filled. Approximately $^1/_5$ of the chloride was left in the original flask and rejected. The more volatile portions, which it was hoped contained the bulk of the hydrochloric acid, were collected in the 3 small bulbs and also were discarded.

The flask containing the partially purified tetrachloride was now attached to a system consisting of one large bulb, 14 small ones and a liter reservoir. After this system also had been carefully evacuated, connection with the flask containing the tetrachloride was made by breaking the capillary in the special joint. The reservoir was first sealed off and then about $^4/_5$ of the liquid was distilled into the first bulb. The bulb containing the residue was next sealed off, and then the small bulbs were successively filled with the tetrachloride and sealed off.

The distillation apparatus was constructed wholly of glass and resembled very closely that used by Baxter and Starkweather in the preparation of tin tetrachloride.[2]

Method of Analysis.[3]

After being weighed the bulb containing silicon tetrachloride was broken under excess of sodium hydroxide and the glass was collected and weighed. The solution was diluted to considerable volume and made acid with nitric acid, and then was precipitated with a solution of a weighed very nearly equivalent amount of pure silver. The point of exact equivalence between chloride and silver was then found with the assistance of a nephelometer.

Water, nitric acid and silver were purified by the usual methods where extreme refinement is necessary.[4] To prepare sodium hydroxide free

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[1] *J. Chem. Soc.*, **107**, 63 (1915).

[2] *Proc. Nat. Acad. Sci.*, **2**, 718 (1916); THIS JOURNAL, **42**, 907 (1920).

[3] The analytical operations were performed by Mr. Weatherill.

[4] See for instance Baxter and Grover, THIS JOURNAL, **37**, 1028 (1915).

from chloride, the best commercial material was precipitated with a slight deficiency of barium hydroxide to eliminate the greater part of the carbonate, and after the precipitate had been thrown out by centrifugal whirling, the clear solution was evaporated to crystallization in a platinum dish. The crystals were centrifugally drained and rinsed and then were twice more crystallized in the same way. The product was free from chloride.

The bulb was cleaned by means of sodium hydroxide and cleaning solution. Then it was rinsed, dried with a lintless cloth and left in a desiccator for some hours before being weighed by substitution. Simultaneously with the weighing, the temperature, pressure and humidity of the balance room were observed. Next the bulb, suspended in a platinum wire basket, was weighed under water and its volume calculated from the weight of water displaced.

The bulb, with a solution of about 50% excess of the quantity of sodium hydroxide necessary to react completely with the tetrachloride, was placed in a heavy-walled glass-stoppered flask, and by shaking the flask the bulb was broken. In order to avoid loss of silicon tetrachloride or hydrochloric acid vapor, the flask was allowed to stand closed for some time. Then it was opened, and after dilution of the solution to one liter, the glass was collected upon a quantitative filter, the solution being received in a large glass-stoppered precipitating flask or bottle. Gentle ignition below the melting point of glass in a weighed platinum crucible eliminated the filter.

The weight of glass determined in this way was found in 5 experiments to be slightly too large. In these experiments a weighed empty bulb was broken under a similar solution of silicon tetrachloride in sodium hydroxide, and then the glass was collected on a filter, washed with cold water, and ignited in an identical fashion. The average excess in weight was 0.20 mg., the largest being 0.34 mg. and the smallest 0.14 mg. A correction of 0.20 mg. has, therefore, been subtracted from the weight of glass found in each of the analyses. A vacuum correction of +0.00034 g. per gram of glass also has been applied.

The weight of the bulb was corrected to vacuum by computing the weight of air displaced by the bulb and weights, with due consideration of the atmospheric conditions at the time of weighing.

As soon as the alkaline solution had been filtered it was made slightly acid with nitric acid, for such acid solutions remain perfectly clear for long periods. From the weight of silicon tetrachloride the necessary amount of silver was computed, and this quantity of the purest silver was weighed out and dissolved in nitric acid. Both solutions having been diluted until approximately 0.1 N (except in Analysis 1), the silver solution was slowly added to the chloride, and the mixture was thoroughly shaken and allowed to stand several days with occasional shaking. The clear supernatant liquid was next tested for excess of chloride or silver in a nephelometer and if a deficiency of either was found, a suitable amount of a 0.01 *N* solution of silver nitrate or potassium chloride was added and the shaking and testing were repeated. The process was continued until the amounts of chloride and silver were equivalent.

The weight of silver has been corrected to vacuum by subtracting 0.031 mg. per gram of metal. The atomic weights of silver and chlorine were assumed to be 107.880 and 35.457 respectively.

In the table the fractions are numbered in the order in which the bulbs were filled. In Analysis 1 the solutions were considerably more concentrated than 0.1 *N* when precipitation was carried out. The apparent effect of this was the occlusion by the precipitate of some of the chloride which slowly leached out, so that the end-point was not finally reached for some weeks. If this leaching out was not complete it would account for the somewhat higher result of this experiment. On the whole, however, the different fractions show no positive evidence of dissimilarity.

Number of analysis.	Fraction of $SiCl_4$.	Weight of $SiCl_4$ in vacuum. Grams.	Weight of silver in vacuum. Grams.	Weight of silver added in solution. Gram.	Corrected weight of silver in vacuum. Grams.	Ratio $SiCl_4$: 4 Ag.	Atomic weight of silicon.
1	12	10.43530	26.47403	0.02120	26.49523	0.393856	28.129
2	3	5.97853	15.17909	0.00395	15.18304	0.393764	28.089
3	9	8.79053	22.31981	0.00150	22.32131	0.393814	28.112
4	6	6.83524	17.35557	0.00060	17.35617	0.393828	28.114
					Average,	0.393815	28.111

While we wish to emphasize the fact we do not consider the evidence presented as final, it seems to indicate that the atomic weight of silicon is not far from 28.1 instead of the value 28.3 as now accepted by the International Committee on Atomic Weights.

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THE CHEMICAL COMPOSITION OF COTTONSEED OIL.

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Although cottonseed oil has been an important article of commerce for a great many years, neither its qualitative nor quantitative chemical composition has been definitely established. Investigators agree that palmitic acid is the predominating saturated acid but the presence of stearic and arachidic acids has been asserted and denied. Hehner and Mitchell[1] found 3.3% of stearic acid in cottonseed oil stearine. Meyer[2]

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[1] Hehner and Mitchell, *Analyst*, 21, 328 (1896).

[2] Meyer, *Chem. Ztg.*, 31, 793 (1907).