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Abstract

Full Text

PHYSICAL CHEMISTRY

G. G. DEVYATYKH, G. K. BORISOV, and A. M. PAVLOV

ON THE SEPARATION OF SILICON ISOTOPES BY RECTIFICATION OF MONOSILANE

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Silicon has three stable isotopes, which occur in natural silicon in the following proportions: Si^{28} 92.27%; Si^{29} 4.68%; Si^{30} 3.05% ([1]).

In small quantities, separation of silicon isotopes has been carried out by the method of electromagnetic separation ([2,3]).

It may be expected that physicochemical methods, which have proved very effective for the separation of isotopes of many light elements, will be applicable to the separation of silicon isotopes. However, so far not a single such method has been proposed. An attempt at separation by rectification of silicon tetrachloride proved unsuccessful ([4]). As calculations have shown, the equilibrium constant of the isotopic exchange reaction

$$Si^{28}F_4 + Si^{30}F_6^{2-} \rightleftharpoons Si^{30}F_4 + Si^{28}F_6^{2-},$$

which at present could be used for separation purposes, is very small and is only 1.002 at 27° C ([5]).

The aim of the present work was to investigate the possibility of separating silicon isotopes by rectification of monosilane. Monosilane has a low boiling point, and the relative mass difference of its isotopic molecules is the greatest among all silicon compounds. Therefore one may expect that the difference in vapor elasticity of silicon isotopes in the form of monosilane is more pronounced than in other compounds.

Fig. 1. Diagram of the rectification column. 1—condenser, 2—vacuum jacket, 3—column, 4—glass cube, 5—viewing windows, 6—ampoules for sample collection.

Fig. 2. Run-up curve for silicon isotopes: a–$Si^{29}H_4$, b–$Si^{30}H_4$

Figure 2: Fig. 2. Run-up curve for silicon isotopes: a–$Si^{29}H_4$, b–$Si^{30}H_4$

The distillation of monosilane was carried out in a packed metal rectification column, the scheme of which is shown in Fig. 1. The packing consisted of spirals measuring 2×2 mm made of nichrome wire 0.18 mm in diameter. The height of the packing layer was 240 cm. The column diameter was 10 mm. The efficiency of the column, determined from the separation of carbon isotopes during rectification of carbon monoxide, was 60 theoretical plates. The distillation was carried out at a monosilane pressure of 560 mm Hg, which corresponds to $-117°$. The samples of monosilane withdrawn during distillation for isotope analysis on the mass spectrometer were converted into silicon tetrafluoride.

This conversion was carried out as follows. Monosilane was burned in an oxygen atmosphere to silicon dioxide, which was dissolved in hydrofluoric acid; by the action of barium chloride on the solution, a precipitate was obtained.

barium silicofluoride; by thermal decomposition of it, silicon tetrafluoride was obtained.

Mixtures of monosilane with oxygen containing less than 50% monosilane are stable at atmospheric pressure and room temperature, whereas mixtures containing more than 50% monosilane are explosive under the same conditions (6-8). For the reaction of monosilane with oxygen to proceed calmly, hydrogen peroxide was used as the initiator. Dissolution of silicon dioxide and precipitation of barium silicofluoride were carried out in a polyethylene beaker. The precipitate was washed with distilled water, transferred to a porcelain crucible, and dried at 120°. After this the precipitate was placed in a stainless-steel test tube. To remove traces of water, the test tube with the precipitate was heated to 250° and pumped by a mercury diffusion pump to a residual pressure of $\sim 5 \cdot 10^{-5}$ mm Hg; then the pump was switched off and the test tube was heated to $\sim 800°$. Under these conditions barium silicofluoride decomposed with liberation of silicon tetrafluoride.

Fig. 2. Run-up curve for silicon isotopes: a–$Si^{29}H_4$, b–$Si^{30}H_4$

Isotopic analysis of the samples was carried out on an MI-1305 mass spectrometer. Measurements were made on the ions $Si^{28}F_3^+$, $Si^{29}F_3^+$, $Si^{30}F_3^+$, which correspond to masses 85, 86, 87. Each analysis included no fewer than 8-10 recordings of all three masses.

In processing the mass-spectrum records, in order to take into account small gradual changes in the intensities of the ion currents, interpolation of the heights of peaks 86 and 87 to the time of recording peak 85 was carried out (4).

From the mass spectra the isotopic ratios were found:

$$A_1 = I_{86}/I_{85} \quad \text{and} \quad A_2 = I_{87}/I_{85},$$

where I_{85}, I_{86}, I_{87} are the intensities of the ion currents corresponding to masses 85, 86, 87.

The separation factor was found as the ratio of the isotopic ratios in samples taken from the still and the condenser of the column at the same time,

$$F_{29} = A_1^{\text{still}}/A_1^{\text{cond}}, \quad F_{30} = A_2^{\text{still}}/A_2^{\text{cond}},$$

where F_{29} is the separation factor for the isotope Si^{29}, and F_{30} is the separation factor for the isotope Si^{30}.

The results of the run-up are presented in Table 1 and in Fig. 2. As can be seen from Table 1 and Fig. 2, a stationary state was reached in the column—

Table 1

Results of the rectification of monosilane

Sample No.	Duration of operation, h	F_{29}	F_{30}	Sample No.	Duration of operation, h	F_{29}	F_{30}
1	2.3	1.006 ± 0.004	1.011 ± 0.004	5	20.75	1.019 ± 0.003	1.030 ± 0.004
2	7.1	1.010 ± 0.003	1.012 ± 0.003	6	27	1.012 ± 0.002	1.029 ± 0.002
3	12.3	1.007 ± 0.003	1.016 ± 0.003	7	31	1.022 ± 0.004	1.037 ± 0.004
4	16.3	1.012 ± 0.002	1.024 ± 0.002	8	33.5	1.020 ± 0.004	1.035 ± 0.004

state. From the distillation data, separation coefficients were calculated, equal to the relative vapor pressure of the isotopic varieties of monosilane,

$$\alpha_{29} = P_{Si^{28}H_4}/P_{Si^{29}H_4} = 1.00035 \pm 0.00007,$$

$$\alpha_{30} = P_{Si^{28}H_4}/P_{Si^{30}H_4} = 1.00061 \pm 0.00010.$$

In conclusion, we express our gratitude to L. P. Korovin for assistance in carrying out the experiment.

Research Institute of Chemistry
at Gorky State University
named after N. I. Lobachevsky

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Note: Figure translations are in progress. See original paper for figures.