## *Fractionation of Sulfur Isotopes during Reduction**

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(Received February 10, 1958)

The experimental and the theoretical studies are being made by the present authors on the natural abundance and their variation of stable isotopes of sulfur. In the previous report[1] a great fractionation of the heavy isotope ($^{35}S$) during oxidation of sulfide was reported. The present experiment has been carried out to make clear the fractionation of sulfur isotopes during reduction using sulfur-35 as tracer.

Barium sulfate labelled with sulfur-35 was reduced in a carbon dioxide stream with tin(II)—strong phosphoric acid reagent[2]. Hydrogen sulfide evolved from the reaction mixture was taken out of the reaction system with carbon dioxide. This gas was led to two absorbing cells in series. In the first cell, was placed an accurate, known amount of aqueous zinc acetate solution just enough to make precipitate of zinc sulfide for the radioactivity measurement. In the second cell, alkaline suspension of basic cadmium carbonate was put in to absorb and detect the rest of hydrogen sulfide which comes out from the first cell. The detection of hydrogen sulfide coming in the second cell was easily made by observing the formation of yellow cadmium sulfide. When sufficient zinc sulfide was obtained, the gas-flow of hydrogen sulfide and carbon dioxide from reaction system was switched to another set of two absorbing cells using a three-way stopcock.

In this way, many fractions of small and equal amount of zinc sulfide were obtained. The specific counting rate of each sample was measured by the infinite-thickness method. In order to be sure to detect a small variation in the specific counting rate, hydrogen sulfide evolved in the very beginning of the reaction was carefully sampled, and sixty fractions were obtained during a run of reduction experiment. Some of the results obtained are shown in Fig. 1. There found a regular and remarkable variation in their specific counting rate and the earlier

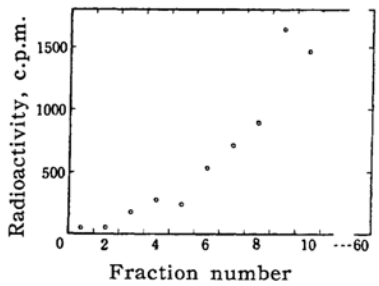


Fig. 1. Variation in radioactivity of each fraction of zinc sulfide obtained in succession from one barium sulfate sample by fractional reduction.

sulfide obtained in a series of a fractional reduction from barium sulfate has remarkably smaller specific counting rate than that in the later stage over the possible experimental error.

The fractionation of sulfur isotopes during oxidation was previously reported[1]. In this case, the radioactive sulfur isotope ($^{35}S$) was enriched in the products of earlier stage of oxidation. Thus the result agrees with the conclusion shown in the present report.

As the fractionation of radioactivity is quite remarkable in both reduction and oxidation, it would be possible to apply successfully in a larger scale to the purpose of enriching stable isotopes as well as radioactive ones. An experiment is planned to determine the extent of the differentiation between the stable isotopes of sulfur-32, 34 and 36 in the same sort of treatment of sulfur compounds.

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* Presented by H. Shimojima before the 8th Annual Meeting of the Chemical Society of Japan on April 3, 1955.

1) I. Iwasaki, H. Fukutomi and H. Shimojima, This Bulletin. **31**, 495 (1958).
2) T. Kiba and I. Kishi, ibid. **30**, 44 (1957).