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Silicon Isotope Separation by Distillation of Silicon Tetrafluoride

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Abstract

Silicon isotopes were separated by distilling silicon tetrafluoride in a 150-cm packed column at temperatures of 189–206 K. The data show a reverse isotope effect with heavy isotopes more volatile in this temperature range. At total reflux, the maximum column separations were 0.926 for $^{28}Si/^{29}Si$ and 0.872 for $^{28}Si/^{30}Si$. Carbon monoxide was also distilled in the column to obtain an estimated number of separating stages. From an estimated HETP of 2 cm for the packing, the volatility of ^{28}Si is 0.9990 relative to ^{29}Si and 0.9982 relative to ^{30}Si. The SiF_4 isotope effect is the largest yet found in distilling silicon compounds, and the effect is opposite that seen for SiH_4. The magnitude of the isotopic relative volatilities is large enough to consider SiF_4 distillation as a practical method for silicon isotopic enrichment. This effect of higher mass isotopes being more volatile has analogues in isotope effects in SF_4 and BF_3.

INTRODUCTION

Natural abundances of the three stable isotopes of silicon are: ^{28}Si, 92.23%; ^{29}Si, 4.67%; and ^{30}Si, 3.10%. The ^{29}Si isotope has a nuclear spin of +1/2 and has potential for nuclear magnetic resonance studies. Separated silicon isotopes are of interest in geochemistry and ceramics because silicon is ubiquitous in the geosphere. Presently electromagnetic separation is the standard method for practical silicon isotope separation (*1*), and highly enriched isotopes (95%) cost about $26,000/g for ^{29}Si and $46,000/g for ^{30}Si (*2*). As a result, relatively small amounts of separated silicon isotopes are used in research. These high costs strongly suggest the need for an alternative technique for producing separated silicon isotopes.

When a sizable vapor–liquid isotope effect can be found, isotope separation by distillation is a process which can be operated at any production scale, often at lower costs than alternative processes. Other investigators have found small isotopic separations of silicon by distilling silane (*3*), silicon tetrachloride (*4, 5*), and methyl silane (*6*). This work was directed toward finding an isotope effect in the vapor–liquid equilibrium of pure silicon tetrafluoride.

APPARATUS

The experimental distillation column is shown schematically in Fig. 1. The separating column is a stainless steel tube, 1.5 m long by 14 mm i.d., filled with stainless steel wire helix packing (Heli-Pak #3013, 1.3 mm by 2.5 mm by 2.3 mm, Podbielniak, Inc.). The packing is supported at the bottom and held down at the top by stainless steel screens. The boiler and condenser are each 15 cm long by 15 mm i.d. nickel-plated copper cylinders and are silver-soldered onto the column. A helium refrigerator (CTI-Cryogenics Model 1050) capable of providing 140 W of refrigeration at 150 K is bolted and thermally bonded to the condenser by a thin sheet of indium foil. To minimize thermal heat leaks, the column assembly is housed in a vacuum jacket, and the column is wrapped with 50 layers of aluminized Mylar. Pressure in the vacuum jacket is maintained below 1 mtorr, and the calculated thermal heat leak to the packed portion of the column is less than 0.1 W.

The temperature of the column is controlled by a thermal balance between column heaters and the refrigerator. A 150-W band heater on the boiler and a 100-W band heater on the condenser run at constant power, varied by autotransformers. Temperatures are measured by copper-constantan thermocouples soft-soldered to the boiler heater and to the column midpoint and by silicon diodes bolted to the boiler bottom and to the side of the condenser. Temperatures are read from Honeywell Dialapak controllers (thermocouples) and a Lake Shore Cryotronics Model DI-8 Cryogenic Thermometer (diodes). High temperature power cutoff protection is provided by the Honeywell controller connected to the boiler heater thermocouple.

The gas-handling manifold (Fig. 2) includes a 10,000-torr pressure transducer (MKS Baratron Model 127AA), a 300-cm^3 trap, a 3-L ballast volume, and valves necessary for gas handling and sampling. Volumes,

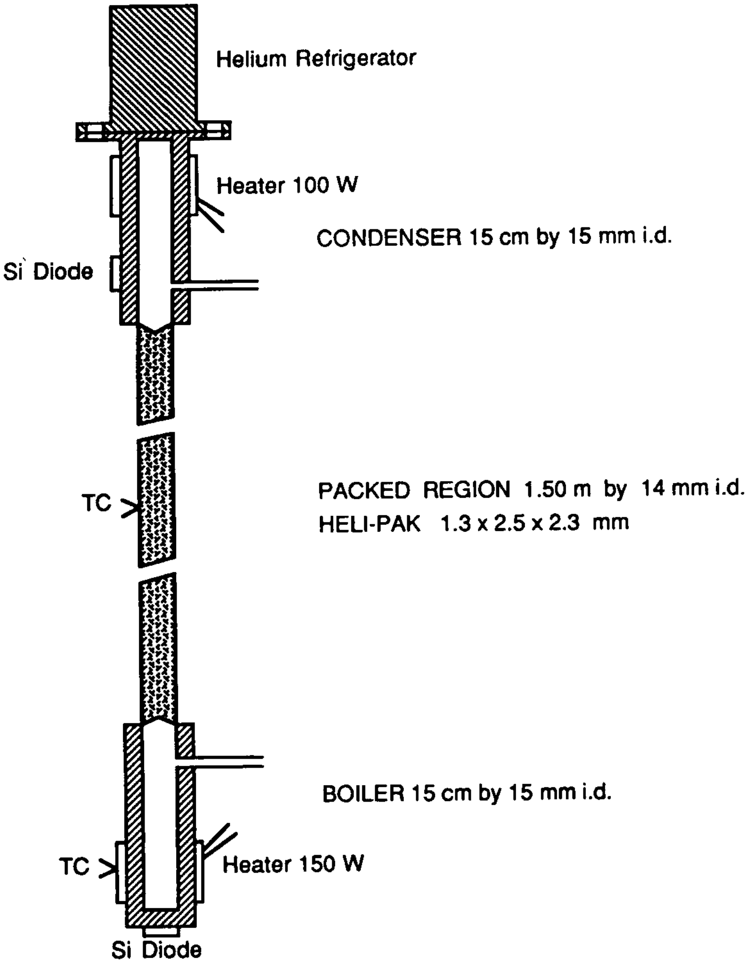

FIG. 1. Isotope distillation column.

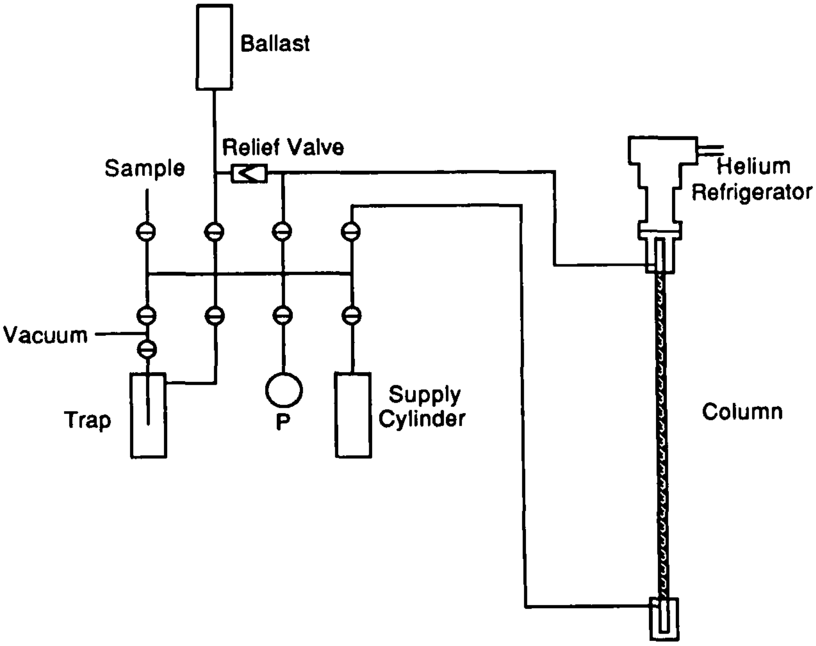

FIG. 2. Gas-handling manifold.

lines, and valve bodies are made of type 316 stainless steel; elastomers used in the system are Viton and Teflon. A relief valve set at 50 psig protects the column from overpressurization by venting into the 3-L volume.

EXPERIMENTAL

When the helium refrigerator was started with the column evacuated, the condenser cooled to 20 K within 1 h; however, the column and boiler remained at essentially room temperature. To speed the removal of heat from the column and boiler, the column was filled with purified SiF_4 at ~2000 torr prior to cooling. (Silicon tetrafluoride sublimes at atmospheric pressure, thus elevated pressure is needed to ensure the presence of liquid.) The condenser heater was adjusted to maintain a condenser temperature above the SiF_4 melting point (183 K).

To minimize introduction of impurities into the column, SiF_4 from lecture bottles (99.6% purity, Linde) was frozen in the 300-cm^3 trap with liquid nitrogen, and volatile impurities were pumped away. The trap was then warmed slowly and kept at low pressure (2000–3000 torr) to retain less volatile impurities in the trap while feeding the column. Any addition of SiF_4 to the column was done through the bottom gas line to minimize the chance of depositing solid impurities in the condenser. When the boiler reached liquid SiF_4 temperature, power was added to the column boiler. It was necessary to maintain power to the condenser heater to avoid freezing SiF_4 at the condenser.

Early runs were made without attempting to obtain maximum packing efficiency. For later measurements, the column packing was totally filled (flooded) with liquid SiF_4 to get proper wetting of the Heli-Pak. At flooding, the pressure drop through the packing was 175 torr, corresponding to the static pressure head from a 1.49-m column of liquid SiF_4 [$\rho = 1.598$ g/cm^3 at $-80°C$ (7)]. The packing was then deflooded by removing SiF_4 gas from the column top at a slow rate over a 4-h period. During the flood/deflood procedure, the boiler power was held constant to maintain the refluxing action which keeps the liquid film on the packing.

Isotopic analyses were done on a Nuclide 12-90-GQ magnetic sector mass spectrometer. The $Si^{19}F_3^+$ ions at m/e 85, 86, and 87 were monitored to obtain isotopic compositions. This was the strongest set of isotope peaks for SiF_4, and the spectrometer had no background peaks at these masses. Data from a minimum of 5 scans of each sample were averaged, and isotopic composition ratios were computed from the 85/86 and 85/87 peak ratios. Any influence due to spectrometer memory of previous gas samples was minimized by pumping the spectrometer well between samples. Duplicate sets of samples yielded the same separation, and the sequence of running top and bottom sample pairs did not affect results.

All measurements of isotopic separation were made with the column at total reflux. Liquid holdup of the packing was monitored by pressure drop through the packing. The ΔP was 2–10 torr, and it slowly dropped from run to run due to gas removed during sampling. Column pressure and temperature were dependent upon power to the boiler and condenser heaters. Over any 24-h period, pressure and temperature went through very slow variations of up to 100 torr and 1 K. Column boilup ranged from 17 to 22 W, corresponding to 3.3 to 4.2 mol/h SiF_4. Following a change in heater power, stable pressure and temperature were reached within 2 h. The column was then allowed to reflux for at least 24 h before sampling. Sampling lines were first purged to remove stagnant gas (0.7

mmol for top line, 1.5 mmol for bottom), then top and bottom gas samples were collected for analyses. Isotopic separations observed after 1 day were unchanged in samples taken on successive days, thus 24 h was sufficient for isotopic concentrations to reach steady-state. No attempts were made to measure transient concentrations.

RESULTS

Measured isotopic separations are given in Table 1. The overall column separation, A, is the quotient of top and bottom isotopic ratios.

$$A_{28/29} = (85/86)_{\text{top}}/(85/86)_{\text{bot}} \tag{1}$$

$$A_{28/30} = (85/87)_{\text{top}}/(85/87)_{\text{bot}} \tag{2}$$

In all runs the ^{30}Si and ^{29}Si are more volatile than the ^{28}Si isotope. This is a reverse isotope effect, as lighter isotopes are more volatile in many simple compounds. The ^{28}Si/^{30}Si separation is nearly the square of the ^{28}Si/^{29}Si separation, which is predicted for three isotopes separated by the same mass difference (*8*). Runs 1-5 were made before the packing was preflooded, and the data show the typical behavior of approximately half the separation without proper Heli-Pak wetting. Pressures of Runs 1-5 were measured on a Bourdon gauge and are less accurate, hence the parentheses.

Following the SiF_4 experiments, carbon monoxide was distilled in the column to obtain a calculational basis for number of theoretical plates in the column. Preflooding was also done for CO experiments. Column top and bottom samples were analyzed for m/e peaks 28 and 29, corresponding to $^{12}C^{16}O$ and $^{13}C^{16}O$. (The mass 29 peak also includes some $^{12}C^{17}O$, but this was ignored because the fraction is small, and it tends to further cancel when the quotient of top and bottom isotopic ratios is taken.) Data from CO runs are given in Table 2. Relative volatilities are computed from the work of Johns (*9*).

The relationship between relative volatility, α, and overall column separation at total reflux is given by

$$A = \alpha^N \tag{3}$$

TABLE 1
SiF_4 Experimental Data

Run	Pressure (torr)	Temperature (°K)	$85/86_{top}$	$85/86_{bot}$	$85/87_{top}$	$85/87_{bot}$	$A_{28/29}$	$A_{28/30}$
1	(1700)	189	17.646	18.292	25.934	28.058	0.9647	0.9243
2	(1900)	190	17.235	17.905	24.802	26.795	0.9626	0.9256
3	(2100)	192	19.305	20.072	27.755	30.166	0.9618	0.9201
4	(1900)	190	19.486	20.325	28.401	30.950	0.9587	0.9176
5	(1800)	190	19.399	20.446	28.289	30.760	0.9488	0.9197
6	2201	193	19.354	20.589	28.523	32.206	0.9400	0.8856
7	2034	192	19.312	20.580	28.596	32.248	0.9384	0.8868
8	1952	191	19.365	20.747	28.604	32.541	0.9334	0.8790
9	4303	206	19.474	20.855	28.893	32.584	0.9338	0.8867
10	2534	196	19.410	20.743	28.769	32.573	0.9357	0.8832
11	2645	197	19.619	21.097	28.835	32.982	0.9299	0.8743
12	2831	199	19.527	21.093	29.326	33.625	0.9258	0.8721
13	2978	200	19.569	20.916	29.412	33.456	0.9356	0.8791
14	3052	200	19.489	20.868	29.231	33.190	0.9339	0.8807

TABLE 2
CO Experimental Data

Run	Pressure (torr)	Temperature (°K)	$A_{28/29}$	$\alpha_{28/29}$	$N_{28/29}$
1	500	79	1.809	1.0075	79
2	439	78	1.864	1.0078	80

where N is the number of theoretical plates in the column. Taking the average of 80 plates for the ^{13}CO data, the column has a HETP for CO of 1.9 cm. This is in agreement with the 2.0-cm plate height for CO isotope plants (*10*).

DISCUSSION

Taking the HETP for the packing to be the 2 cm normally seen for CO, the number of plates is 75 and the maximum observed α's are 0.9990 for $^{28}Si/^{29}Si$ and 0.9982 for $^{28}Si/^{30}Si$ (Run 12). In previous work with Heli-Pak columns, larger HETP's have been observed for compounds other than CO. A HETP of 2.7 cm was found for neon isotope distillation with the same packing and diameter column (*11*). Based upon this experience it is possible that the column may actually have less plates than 75 when SiF_4 is distilled, and computed α's are conservatively low.

These relative volatilities are compared with other measured α's in Table 3. The important factor in comparing isotopic relative volatilities is the absolute value of $\alpha - 1$, also known as ε. The isotope effect in SiF_4 distillation is more than twice as large as that for any other silicon compounds. For comparison to a practical separation system, α for $^{12}C^{13}C$ in CO is about 1.007 (*9*). Carbon monoxide distillation columns built and operated at Los Alamos have produced 10–15 kg/yr at 99% enrichment

TABLE 3
Silicon Isotopic Relative Volatilities

Compound	$\alpha\,^{28}Si/^{30}Si$	Ref.
SiH_4	1.00061	*3*
$SiCl_4$	0.99964	*5*
SiH_3CH_3	0.99935	*6*
SiF_4	0.9982	This work

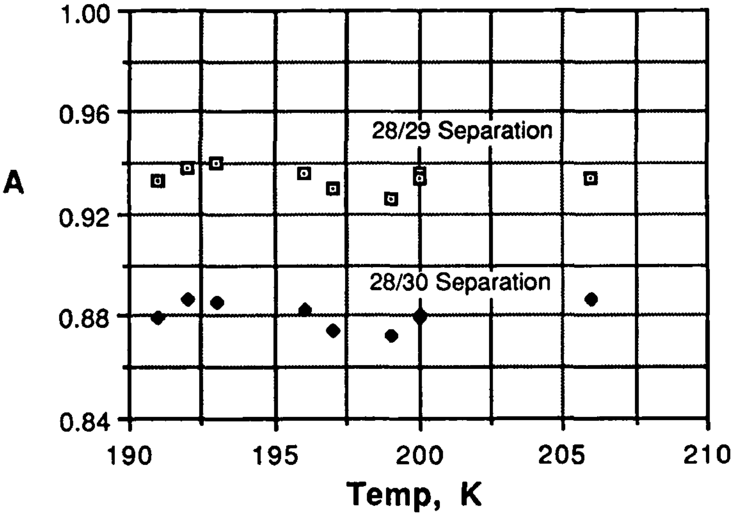

FIG. 3. Total isotope separation in SiF_4.

(*12*). The carbon α is greater than that for silicon by a factor of 4 (for ^{30}Si), but the heavy Si isotopes are several times as abundant as ^{13}C (1.1% natural enrichment).

A clear dependence of relative volatility on temperature is not discernable (Runs 6–14, Fig. 3). For many simple compounds a T^{-2} dependence of ln α is both predicted theoretically (*8*) and found. However, for reverse isotope effects the temperature dependence may be more complicated. For example, α for SiH_4/SiD_4 is >1 for low temperature, becomes a reverse effect ($\alpha < 1$) at higher temperatures, and goes through a minimum and approaches unity as temperature increases further (*13*). The temperature range of the SiF_4 data may correspond to such a minimum, where there is little apparent temperature dependence of α.

The so-called reverse isotope effect is normally not found in common, low molecular weight compounds (e.g., CO, NO, H_2S); however, it occurs regularly for polyhalogenated compounds. The higher volatility of ^{11}B in BF_3 is well known (*14*). Although $^{13}CH_4$ has the normal isotope effect (*9*), $^{13}CHF_3$ exhibits a small reverse effect (*15*). The $^{32}S/^{34}S$ volatility in SF_4 is 0.9992 at atmospheric pressure (*16*). Russian investigators have observed a $^{46}Ti/^{50}Ti$ volatility in $TiCl_4$ of 0.996–0.998 (*13*). From the above, a rule of thumb is to expect a reverse isotope effect for the central atom of simple, polyhalogenated compounds.

CONCLUSIONS

The measured silicon isotope separation in the experimental column, while small, is sufficiently large to consider its use in a practical separation of Si isotopes. (In general, a compound with an ε of absolute value $\geqslant 0.001$ is worth considering for isotopic distillation.) The precise measurement of SiF_4 relative volatilities requires either measuring the isotopic separation in a single equilibrium stage or measuring total column separations under varying flow conditions. However, the total column separations are *actual* separations in an *actual* column. If longer columns with the same packing are used, silicon isotopic separations may be accurately projected from these data. The reverse isotope effect in SiF_4 follows the pattern observed in other halogenated compounds. Work is continuing with SiF_4 and other silicon compounds to seek improved separations and understanding of the reverse effect.

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