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Vapor Pressures and Exchange Constants of Isotopic Compounds

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and 2 percent sodium sulfite by weight, and by operating at a pressure of 10 cm of mercury.

Under these conditions, the column reached equilibrium in about eight hours without a trace of polymer being formed. The ratio of the carbon isotopes was changed by a factor of 1.84 and the ratio of nitrogen isotopes by a factor of 1.09 in the opposite direction. Assuming 40 theoretical plates in the column on the basis of previous experiments on the ammonia-ammonium ion exchange, the simple process factor for the hydrogen cyanide-cyanide ion exchange is calculated to be 1.015 favoring the concentration of C^{13} in the gas phase. The equilibrium constants for the exchange of carbon and nitrogen in this reaction were calculated by the method of Urey and Greiff,[6] assuming the structure of cyanide ion to be that of a gas. These calculations predict that both C^{13} and N^{15} should concentrate in the gas phase by factors of 1.026 and 1.003, respectively. This is qualitatively in agreement with the above experiments in that C^{13} shows a greater tendency than N^{15} to concentrate in the gas phase.

We are planning to use this exchange reaction to concentrate C^{13}. The cascade system of columns described by Thode and Urey,[2] modified to concentrate an isotope favored in the gas phase, should produce 46 percent C^{13} at the rate of two grams per day.

We are indebted to the Research Corporation for a grant which aided in construction of the column and analytical apparatus used in this research.

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[1] J. R. Huffman and H. C. Urey, Ind. and Eng. Chem. **29**, 531 (1937).

[2] H. G. Thode and H. C. Urey, J. Chem. Phys. **7**, 34 (1939).

[3] H. G. Thode, J. E. Gorham and H. C. Urey, J. Chem. Phys. **6**, 296 (1938).

[4] Unpublished work in this laboratory.

[5] U. S. Patents Nos. 1,856,606 and 1,950,899. We are indebted to the duPont Company for permission to use these patents.

[6] H. C. Urey and L. J. Greiff, J. Am. Chem. Soc. **57**, 321 (1935).

Vapor Pressures and Exchange Constants of Isotopic Compounds*

During the past few years a number of experiments have been made in this laboratory looking toward methods for the concentration of rare isotopes. Many of these experiments have given negative results, while others have given positive results but the separation secured was too small to make the method interesting for serious work in concentrating isotopes on a large scale. Nevertheless, these experiments may have some interest in connection with general properties of isotopic substances.

TABLE I.

TIME	TEMPERATURE	CONCENTRATION FACTOR
1 hr.	−10°C	1.06
	−40°C	1.11
½ hr.	−80°C	1.18
1¼ hr.	−80°C	1.19

Distillation Methods. The Pegram column[1] was used to distill methyl alcohol to see whether it was possible to separate either the carbon or the oxygen isotopes. After a run of several days O^{18} was doubled in concentration at the bottom of the column, but C^{13} concentration was practically unchanged. The concentration secured shows that the vapor pressure of the O^{16} methyl alcohol is larger than that of the O^{18} alcohol. Formic acid was refluxed using a 1.8-meter column one cm inside diameter, packed with glass spirals for 1½ hours at a temperature of 30° to 35° with no change in the carbon concentration.

Gas Solubility Methods. Attempts were made to secure a separation by dissolving a gas in a liquid, following the general method of procedure used in this laboratory for exchange reactions.[2] CO_2-acetone exchange was carried out in the 1.8-meter one-cm diameter column with no change in the carbon concentration. The $SO_2-C_6H_5NO_2$, SO_2-CH_3OH and SO_2-H_2O exchanges were carried out in the same column with no change in concentration of the sulfur isotopes. The HCl-water exchange was carried out in an 8-meter one-cm diameter column for 44 hours at room temperature and atmospheric pressure, with a resulting slight concentration of Cl^{35} in the liquid. The ratio of concentration was changed by a factor 0.97. The C_2H_2-acetone exchange in the same column gave the results shown in Table I.

The heavy isotope of carbon concentrated in the liquid phase, but the concentration was not sufficient to be interesting as a method of separating C^{13}.

Exchange Reactions. Carbon monoxide exchange with the cuprous chloride-carbon monoxide complex in ammonia, resulted in the deposition of metallic copper and destruction of carbon monoxide. A similar result was secured when acetylene was exchanged with the cuprous chloride-acetylene complex in hydrochloric acid solution. Carbon monoxide exchanging with the cuprous chloride-carbon monoxide complex in hydrochloric acid solution using the 8-meter one-cm diameter column gave a maximum concentration factor of 1.69, concentrating C^{13} in the solution. The hydrogen sulfide exchange with sodium hydrogen sulfide solutions, using the same column, gave a concentration factor of 0.94 favoring S^{34} in the gas.

In all cases of distillation or simple solution exchanges which we have investigated, with the exception of hydrochloric acid in water (which can hardly be regarded as a simple solution exchange), the heavy isotopes of elements other than hydrogen have regularly concentrated in the liquid phase rather than the gaseous phase.

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[2] H. G. Thode and H. C. Urey, J. Chem. Phys. **7**, 34 (1939).