A Concentration of the Carbon Isotope

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A Concentration of the Carbon Isotope

Urey and Greiff[1] pointed out that it should be possible to change the ratio of the isotopes of an element by making use of chemical exchange reactions in conjunction with a counter-current scrubbing apparatus of the type of fractionation columns. In such a method it is necessary to use a two-phase system, gas and liquid. The gas takes the place of the vapor and a solution the place of the liquid in the usual counter-current distillation. Calculations were reported in their paper showing that the equilibrium constants for exchange reactions involving isotopes of the lighter elements, were not exactly unity and in some cases that they differed from unity by as much as nine percent. It was also pointed out that the use of a bicarbonate solution as the liquid phase and carbon dioxide as the gas phase, should be useful for such methods as applied to the carbon isotopes. Though the experiments made to date are not entirely satisfactory, we wish to report them briefly at this time, since difficulties with analytical procedures will delay the completion of our work for some months.

In the initial attempts to make use of the exchange reaction between bicarbonate ion and carbon dioxide, no increased concentrations could be secured. In these experiments a bicarbonate solution was passed through a fractionation column, acid added to the solution at the bottom, and the carbon dioxide passed back through the fractionation column. Since we were not able to calculate the equilibrium constant for this exchange reaction it seemed possible that the equilibrium constant for the reaction was very nearly unity. However, it was called to our attention that the reaction between carbon dioxide and water to give carbonic acid is a slow reaction which is catalyzed by an enzyme, carbonic anhydrase, which can be extracted from red blood cells.

A crude solution of carbonic anhydrase was prepared according to the directions of Meldrum and Roughton,[2] by mixing ox blood cells with 0.4 their volume of ethyl alcohol, 0.6 their volume of water, and then shaken with 0.5 their volume of chloroform. After centrifuging, the supernatant enzyme solution was used directly without further purification.

When the enzyme solution was added to potassium bicarbonate solution, and then used in the way indicated above, an immediate increase of the concentration of C^{13} in the liquid phase was secured. The difference in concentration between this carbon and normal carbon was only a few percent and hence the detection lay just within the limits of the analytical method.

During the past year we have constructed a very efficient fractionation column as described in another letter in this issue. Potassium bicarbonate solution containing about 25 percent by weight of the salt, was pumped into the top of the column by a proportioning pump. At the bottom of the column a cascade of three flasks in series was used to liberate the carbon dioxide. Sulphuric acid was run into the first flask attached directly to the bottom of the column at a constant rate sufficient to neutralize the potassium bicarbonate solution. The flask was heated so that a vigorous evolution of carbon dioxide occurred.

The overflow from this flask passed into a second flask which was heated and the water condensed and run into the first flask. The overflow from the second flask was passed through a third flask arranged in the same way. The overflow from the third flask contained no carbon dioxide that we could detect.

The potassium bicarbonate solution in the first run was passed in at the rate of 50 cc per minute and in a second run at the rate of 100 cc per minute. After 45 hours of steady operation the carbon from the first of these runs analyzed 1.36 percent C^{13} instead of 1.06 percent, which we take as a natural abundance. In the second run at the end of 12 hours operation, the carbon analyzed 1.21 percent. For some reason which we do not understand at present, the contents of the column amounting to approximately 2000 grams of potassium bicarbonate, showed carbon of the same composition as the sample removed from the bottom of the column. This indicates that only a small fraction of the 35-foot fractionation column produced any change in the isotope composition.

The column contained approximately 240 grams of carbon as carbon dioxide and bicarbonate ion. The 0.3 percent increase in concentration means, therefore, that in the first experiment 0.78 gram of C^{13} was transferred from normal carbon to a higher concentration in the course of 45 hours and in the second experiment approximately 0.39 gram was transferred in 12 hours. From this it is possible to estimate the simple process fractionation factor for this method since the net amount transferred to the bottom of the column must be qual to the difference in concentration of carbon in the carbon dioxide escaping and the carbon in the bicarbonate solution entering the column multiplied by the total mass of carbon used in these experiments. Calculating in this way we find that the simple process fractionation factor in the first run is approximately 1.013, and in the second run approximately 1.014. Since it cannot be assumed that equilibrium conditions were maintained at the top of the column throughout the run, the simple process fractionation factor may be larger than these numbers. It is interesting to note that this fractionation factor is approximately the same as that calculated by Urey and Greiff for the carbonate ion-carbon dioxide exchange reaction. Further work is in progress on this exchange reaction.

Though the increased concentration secured in these experiments is small, the fact that only a small fraction of the column must have been operating gives us reason to believe that considerably greater concentrations can be secured eventually. Moreover, the transport of heavy material in these experiments is very much as compared with other methods which have been used. The amounts of C^{13} transported from the low concentration material to the higher concentration are approximately one thousand times as great as those secured by the Hertz diffusion method in the same lengths of time.

We are indebted to Dr. W. W. Lozier for analyses of carbon samples using a mass spectrometer built for us by a grant from the Carnegie Institution of Washington, and also to Dr. Sampson of Princeton University for a certain

number of analyses in connection with these experiments. The apparatus used by him was built from funds furnished by the American Philosophical Society. We should also say that we are indebted to Dr. Walker Bleakney of Princeton University for many courtesies in connection with the analysis of our samples.

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[1] Urey and Greiff, J. Am. Chem. Soc. **57**, 321 (1935).
[2] Meldrum and Roughton, J. Physiol. **80**, 113 (1933).

The Concentration of the Oxygen Isotopes

As Lewis and Cornish[1] showed, there is a difference in vapor pressures of the O^{16} and O^{18} varieties of water. Experiments by Wahl and Urey show that this ratio of vapor pressures amounts to approximately 1.003 at the boiling point of water, and approximately 1.008 at 45° centigrade. This small difference in vapor pressure may be used for the concentration of the O^{16} isotope if sufficiently efficient fractionation columns can be constructed. Simple calculations show that such a column must have approximately 500 theoretical plates in order to produce increased concentrations of the isotopes sufficient to make possible an eventually complete separation of O^{18}. At the time this work was begun no such columns had been devised. One of us (G. B. P.)[2] suggested the use of alternate rotating and stationary cones in order to secure a very long path without making the column prohibitively long. The apparatus as at present constructed is 35 feet long and contains 619 rotating cones and 619 stationary cones. The rotating cones are attached to a shaft placed in the center of a 6″ tube. The stationary cones are attached to the tube. The distance between two stationary cones is ⅜ of an inch and the rotating cones are placed as nearly as possible midway between stationary cones. In this way water drops from a fixed cone to a rotating cone, is carried by centrifugal force up and off to the walls of the tube and then drains under gravity to the center and drops to the next rotating cone. A complete description of this apparatus will be published later.

First experiments were made on a column containing 14 stationary and 14 rotating cones and later with a 5-foot section containing 90 cones of each variety and finally experiments have been made with a 35-foot column as described above. The initial experiment indicated that a theoretical plate is secured for approximately each pair of cones. In the case of the 5-foot section the results were not quite so good, approximately 75 theoretical plates being secured as shown by the separation of the oxygen isotopes of water using the ratio of vapor pressures as determined by Wahl and Urey. Using the 35-foot column a change in the ratios of the oxygen isotopes by a factor of 2 was secured. In these experiments a large container of water was used at the bottom and total reflux was used at the top. In this way water containing less O^{18} than

the natural abundance was produced at the top. It required approximately four days for a stationary state to be established, after which no change in the concentration of the isotopes occurred. This is very much less than was expected on the basis of our experiments with shorter columns. The water in the boiler at the bottom was heated by steam and no careful attempts were made to control the rate of boiling precisely. Approximately 100 cc of water were boiled through the column per unit time and considerable fluctuations were noted in the back pressure on the column.

In the most recent experiments with the 35-foot column a flash boiler has been placed at the bottom of the column capable of boiling approximately 50 cc of water per minute. Water has been pumped into the top of the column with a proportioning pump and the water vapor issuing from the top of the column has been condensed and run to the sewer. The run was made under 20 centimeters pressure at the top of the column and water was introduced at the rate of approximately 45 cc per minute. The apparatus operated steadily, day and night, for eight days. At the end of this time the oxygen isotope concentration at the bottom of the column had been increased by the factor of 3 from the natural abundance and the deuterium content by a factor of approximately 40. These figures would indicate that the column operated at approximately 230 theoretical plates, a considerably smaller number than expected on the basis of preliminary experiments. Considerable difficulty was encountered in keeping the proportioning pump operating steadily because of rust collecting in the valves of the pump. It stopped operation completely on several occasions for periods of time that were unknown since the column was not attended except occasionally during this time. Also, an accident occurred in adjusting the pump which caused it to introduce approximately 150 cc of water per minute for a period of perhaps one hour. Such irregularities are certain to cause a decreased efficiency of the column. Considering these difficulties the increased concentration appears to be as good as could be expected. A steady state was not reached as shown by analyses on the last two days.

Analyses were made by passing water samples mixed with hydrogen over platinized asbestos at a temperature of approximately 350° centigrade to promote the exchange between water and hydrogen. In this way it was possible to bring the concentration of deuterium to very near normal concentration. The water samples were then diluted with distilled water and density difference determined by the pressure float method of Gilfillan.[3]

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[1] Lewis and Cornish, J. Am. Chem. Soc. **55**, 2616 (1933).
[2] G. B. Pegram, Phys. Rev. **49**, 883 (1936).
[3] Gilfillan, J. Am. Chem. Soc. **56**, 406 (1934).