I would like to point out that the "new limitation, that of a reactive halogen on the beta carbon atom," just suggested by Dawson, was first presented in my paper of five years ago.

Coal Research Laboratory Carnegie Institute of Technology Pittsburgh, Pennsylvania

W. R. KIRNER

Vol. 55

•

RECEIVED JULY 12, 1933

A SIMPLE TYPE OF ISOTOPIC REACTION

PUBLISHED AUGUST 5, 1933

Sir:

It was shown by Lewis and Cornish [THIS JOURNAL, **55**, 2616 (1933)] that when water is distilled through a fractionating column, a large separation of the isotopes of hydrogen and oxygen can be effected, especially if the distillation is carried out under reduced pressure. In order to concentrate considerable amounts of these isotopes, Professor Merle Randall has now designed and constructed, in this Laboratory, a large still which has been in operation for about two months. The density of the water at the bottom of the still has been steadily increasing and it is important to know how much of the increase in density is due to H² and how much to O¹⁸. The method used by Lewis and Macdonald [J. Chem. Phys., 1, 341 (1933)] for separating the hydrogen and oxygen of a given sample of water, which consisted in passing the steam over hot iron, is cumbrous. I have therefore sought some simpler process depending upon the interchange of isotopes in an aqueous solution, such as may be exemplified by the reaction

 $H^{1}H^{2}O + NH^{1}H^{1}H^{1} = H^{1}H^{1}O + NH^{1}H^{1}H^{2}$

Ammonia in water may be regarded as forming ammonium hydroxide, and again dehydrating, this process proceeding back and forth with very great velocity. Now the fourth hydrogen of the ammonium group is exactly like the others and when the dehydration occurs, each of the four hydrogens has an equal chance of being lost. Therefore there must be a rapid interchange of such hydrogen isotope as is present so as to give almost immediately a nearly random distribution of the isotope between NH_3 and H_2O . When ammonia gas is passed into water at 0°, one mole of water absorbs nearly one mole of ammonia and since ammonia has three hydrogen atoms, while water has two, more than half of the H² in the system will escape when the ammonia is pumped off.

A sample from the still which showed an excess density (over ordinary water) of 0.000182 was saturated with ammonia at 0° and then the ammonia was pumped off at room temperature. This process was performed six times, at the end of which all but about one per cent. of the accumulated H² should have disappeared if saturation and exhaustion had been complete in each step. However, no pains were taken in these respects

3502

Aug., 1933

so that probably several per cent. remain of the original accumulation of H^2 . After purifying the remaining water its excess density proved to be 0.000085, or in other words, at least 0.000097 of the original excess density was due to H^2 .

Another part of the same sample was treated with sulfur dioxide, which removes the excess of oxygen isotope by a corresponding reaction

 $H_2O^{18} + SO^{16}O^{16} = H_2O^{16} + SO^{16}O^{18}$

In this case the sulfur dioxide was allowed merely to bubble through the water for several days. The excess density of the residue was 0.000109, showing that of the original density excess at least 0.000073 was due to O^{18} . We thus account for 0.000170 of the original 0.000182. This crude experiment shows that with a little refinement we shall have an exact method for analyzing water containing isotopes of both oxygen and hydrogen. In work of precision the isotopic composition of the ammonia must be ascertained, especially if it is prepared from electrolytic hydrogen, and precautions must be taken against any large loss of water by evaporation.

DEPARTMENT OF CHEMISTRY UNIVERSITY OF CALIFORNIA BERKELEY, CALIFORNIA RECEIVED JULY 22, 1933 PUBLISHED AUGUST 5, 1933

THE BIOCHEMISTRY OF WATER CONTAINING HYDROGEN ISOTOPE Sir:

Even before I had succeeded in concentrating the isotope of hydrogen, I predicted that H²H²O would not support life and would be lethal to

higher organisms. As soon as heavy water became available experiments to test this idea were begun, but it was necessary to choose an experiment which would require the minimum of biological technique and also very small quantities of water.

The minute seeds of tobacco (nicotiana tabacum var. purpurea), which Professor C. B. Lipman has kindly furnished me, were found to germinate almost infallibly under favorable conditions. I then placed twelve of these seeds in pairs in

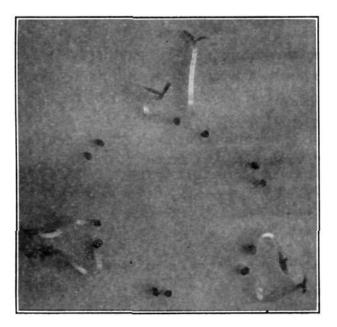


Fig. 1.