dication of such an interchange, even under conditions more drastic than those previously employed.

Each experiment was carried out with 10–15 cc. of water containing about 1.5 mole per cent. of deuterium. The density was determined pycnometrically with an accuracy of 0.002%, so that interchange of hydrogen to an extent of 2% could have been detected with certainty. The acetylene was prepared from calcium carbide and purified by passing through solutions of sodium hydroxide and chromic acid; it was passed continuously through the solutions being investigated at about 500 cc. per hour. In the experiments at 76° the evaporation loss was reduced to less than 5% by a reflux condenser. After removing the acetylene by a current of air or carbon dioxide the solutions were distilled at least twice *in vacuo* at 40–50°, and the density determined. The density was in each case unchanged by repeated distillation, provided that the whole of the water was distilled over. The following experiments were carried out:

N NaOH	Acetylene passed 11 hours at 0°
Pure water	Acetylene passed 5 hours at 76°
N NaCl	Acetylene passed 5 hours at 76°
0.01 *N* $Ba(OH)_2$	Acetylene passed 3.5 hours at 76°
0.1 *N* $Ba(OH)_2$	Acetylene passed 5 hours at 76°
0.5 *N* $Ba(OH)_2$	Acetylene passed 9.5 hours at 76°

In no case was any change in isotopic composition observed. (The hydrogen contained in the hydroxides was taken into account in calculating the original composition.)

These results are completely at variance with those of Reyerson and Yuster, who obtained about 50% interchange on treating *N* sodium hydroxide with acetylene for eight hours at 0°. It is difficult to suggest an explanation for this discrepancy.

PHYSICAL CHEMISTRY LABORATORY R. P. BELL
BALLIOL COLLEGE AND TRINITY COLLEGE
OXFORD, ENGLAND

RECEIVED MARCH 8, 1935

THE ISOTOPIC INTERCHANGE BETWEEN ACETYLENE AND HEAVY WATER

Sir:

Dr. R. P. Bell was kind enough to send me a copy of the communication to the Journal concerning his failure to obtain the isotopic interchange between acetylene and heavy water which we previously had reported. In answer to the question raised by Dr. Bell, I wish to report that under the conditions of our experiments there is no question but that the isotopic exchange takes place. Since our previous publication several equilibrium studies of this reaction have been completed in this Laboratory. They have been carried out at 0, 25 and 100° in closed systems using various pressures of acetylene which was prepared by the action of carefully distilled water on very pure calcium carbide, the acetylene being further purified. The concentrations of deuterium in the water used varied from about 9 to 18%. Except for a small temperature coefficient the equilibrium constants checked excellently. This work is being written up for a lengthier publication on the subject. In addition to the above evidence Mr. A. O. Nier working in Professor J. T. Tate's laboratory in physics has completed an analysis of the products of one of our equilibrium studies by means of the mass spectrograph. He reports that about 10% of the gas submitted for analysis consisted of C_2HD. This checks very well the value calculated from the density change in the water as determined in this Laboratory.

Dr. Bell states in his communication that his experiments were carried out under more drastic conditions than those reported by us. This does not seem to be borne out by the facts. The concentration used in our solutions was from six to eight times as great, and the rate of passage of the acetylene through the solution was approximately seven times as great as that reported by Dr. Bell. Since all but one of his reported experiments were carried out at 76° it must be he considered this to be more drastic treatment. However, in order for the exchange to occur the acetylene must dissolve in the solution and then ionize. The solubility of acetylene is much less at 76° than at zero so that the chance for exchange is thereby reduced. A simple calculation from our equilibrium constant values obtained for the reaction

$$C_2H_2 + HDO \rightleftharpoons C_2HD + H_2O \text{ at } 0°\text{C.}$$

shows that the amount of exchange with 1.5% deuterium should be very small, even under equilibrium conditions, conditions which are obviously not reached by bubbling the gas through the solution for the length of time reported. It seems therefore that Dr. Bell did not lose sufficient deuterium from the water to detect it by the technique he employed. Dr. Yuster in a private communication to the author suggested a further possibility for Dr. Bell's failure to observe the exchange. All of our studies have been carried out in Pyrex glass systems so that there is undoubtedly some borate present in the alkaline solutions. If Dr. Bell's studies were carried out in soft glass then it is possible that the borate acts as a catalyst in the rapid establishment of exchange equilibrium while the soluble substances from soft glass do not act as efficiently.

UNIVERSITY OF MINNESOTA L. H. REYERSON
MINNEAPOLIS, MINN.

RECEIVED MARCH 23, 1935

CONCENTRATION OF TRITIUM (H^3)

Sir:

About a year ago detection of the hydrogen isotope of mass 3 in substantially protium-free deuterium was reported by Lozier, Smith and Bleakney [*Phys. Rev.*, **45**, 655 (1934)]. At that time the tritium concentration was estimated as 5 in 10^6 after the initial volume of ordinary water had been reduced by electrolysis to 1 part in 225,000. Electrolysis has been continued during the past year until the volume has now been reduced to 1 part in 150,000,000. That is, approximately 75 metric tons of ordinary water have been electrolyzed down to 0.5 cc. During this time the tritium concentration as determined by the mass spectrograph has increased to about 1 in 10^4. We are now in a position to obtain the ratio of specific discharge rates of deuterium and tritium, and to estimate the abundance of tritium in nature.

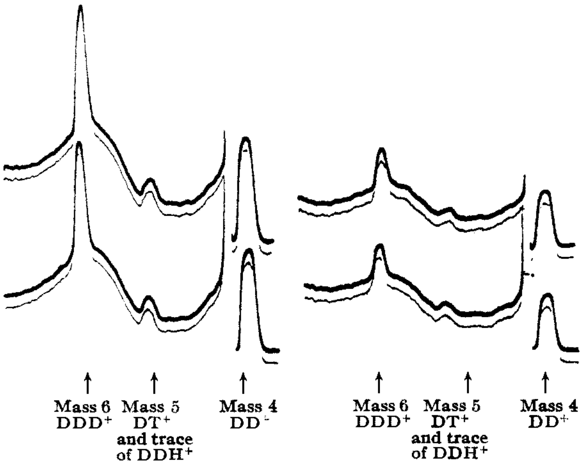

Fig. 1.

The discharge ratio (α_T^D) for deuterium and tritium may be obtained by graphical integration of the total tritium evolved during substantially complete electrolysis of a given sample of protium-free deuterium oxide. The value so obtained is 2.0, in good agreement with the theoretical prediction of Eyring [*Scientific Monthly*, **39**, 415 (1935)]. We have the relation $\alpha_T^H = \alpha_T^D \cdot \alpha_D^H$, and as α_D^H averages about 6 in the Princeton heavy water plant, α_T^H = about 12. In estimating the abundance of tritium in nature it must be borne in mind that during the earlier part of electrolysis, tritium is concentrated chiefly with respect to protium, but during the latter part entirely with respect to deuterium. For the purpose of making a rough computation we assume that α changes from 12 to 2 when the H:D ratio is 1–1. The abundance of tritium in ordinary water is then 7 in 10^{10}.

Figure 1 shows the intensities, recorded automatically, of the ions of masses 6, 5 and 4, the latter on a much reduced scale owing to its great abundance in the mixture. The intensities in the left half of the diagram are at a greater pressure than those on the right. From the pressure influence thus examined over a series of pressures we find that the intensity due to the ion of mass 6 varies as the square of the pressure. It is therefore triatomic and must be DDD^+. The ion of mass 5 varies in intensity nearly directly with the pressure and must therefore be mainly diatomic and hence DT^+. It is from the plot of the intensity–pressure ratio against pressure that, as has been previously described, the atomic content of tritium is deduced. Our results show that by further electrolysis of the deuterium oxide preparations now produced in commercial quantities both in this country and Europe, residues rich in tritium can readily be assembled without significant loss of deuterium since the electrolytic gas so produced can be recombined to yield deuterium oxide from which the tritium has been partially removed.

FRICK CHEMICAL LAB. P. W. SELWOOD
PALMER PHYSICAL LAB. H. S. TAYLOR
PRINCETON UNIV. W. W. LOZIER
PRINCETON, N. J. WALKER BLEAKNEY

RECEIVED MARCH 22, 1935

DEVELOPMENT OF AN AIR-DRIVEN ULTRACENTRIFUGE

Sir:

Up to last summer, Svedberg alone had produced convectionless centrifuges whose contents could be submitted to optical observation while in motion. In 1931, we undertook at Stanford