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RESEARCH ON HEAVY HYDROGEN AT PRINCETON¹

By Dr. HUGH S. TAYLOR

DAVID B. JONES PROFESSOR OF CHEMISTRY, PRINCETON UNIVERSITY

THE heavy water produced in the Frick Chemical Laboratory at Princeton University has been found to possess a specific gravity greater than that recorded hitherto by at least two tenths of one per cent. The value obtained for the specific gravity is 1.1078 at 77 degrees Fahrenheit (25 degrees Centigrade) as compared with the value 1.1056 previously recorded by Professor G. N. Lewis, of California. Many samples of this, the purest heavy water hitherto obtained, have been studied by Dr. P. W. Selwood; in all more than three ounces of heavy water of this gravity has been investigated and further processes of refinement have failed to produce any increased density. The presumption is, therefore, strong that this represents the density of pure deuterium oxide.

This heavy water is the residue from the treatment of upwards of 10 tons of industrial electrolytic liquor, which contains about one part of heavy hydrogen to 2,000 parts of light hydrogen. According to Princeton researches, ordinary rain water contains but one part in 5,000 of the heavy atoms. The Princeton production up to the present time corresponds, therefore, to the treatment of approximately 25 tons of ordinary water, and the present operations consume about two tons of industrial liquor per month, with a daily output of three grams of the 100 per cent. product. The method of preparation used is based upon comparative studies by Professor Eyring and Dr. Topley of the fractionation efficiencies of various electrode surfaces.

The costs of production have been materially lowered so that it is now possible to produce this 100 per cent. heavy water for approximately \$5 per gram, in-

¹ Recorded at the Princeton Sigma Xi Symposium on Heavy Water, March 20, 1934, and in a lecture at the Franklin Institute, March 21, 1934, on "Heavy Hydrogen—A New Research Tool."

cluding materials, labor and electric power costs. In the form of a 1 per cent. solution of heavy water the costs of production approximate one tenth of this amount. By suitable modifications of present large scale industrial production of electrolytic hydrogen and oxygen it is planned still further to reduce this cost and considerably to enlarge output. By the summer it is hoped that 12 to 15 pounds of the purest heavy water will be available for the Princeton researches.

The terrestrial abundance of heavy hydrogen (of mass 2) (1 part in 5,000) is considerably greater than that revealed by astronomical spectrograms. Menzel of Harvard estimates the abundance, as shown in the latter, at less than 1 part in 500,000 and suggested therefore that in the formation of the earth there had been a tremendous preferential loss of the light hydrogen. In collaboration with Professor Henry Norris Russell, of the Princeton Astronomy Department, he has extended this finding to the case of other gases, notably neon. This leads to important conclusions concerning the earliest periods of terrestrial history.

The announcement by Lord Rutherford of the possible synthetic production of hydrogen by mass 3 (tritium) by bombardment experiments with high-speed deuterons gives interest to a joint research in the laboratories of physics and chemistry by Dr. Bleakney and Mr. Gould. Using the mass spectrograph it has been shown that the amount of hydrogen of mass 3 present in ordinary water can not exceed 1 part in 500 millions; even in the purest heavy water thus far obtained the concentration of this third hydrogen is less than 1 part in 50,000.

Conclusions of importance in the field of chemical reactions at surfaces, especially in such industrially important fields of catalysis as the synthesis of ammonia and wood alcohol, have resulted from studies carried out by Mr. Gould under the direction of Professor Hugh S. Taylor of the chemistry department. It has been shown that light hydrogen molecules (H_2) will react with deuterium molecules (D_2) to produce mixed molecules (HD), at temperatures as low as that of liquid air, with catalysts, such as chromium oxide. These results indicate that the high temperatures necessary in industrial syntheses are required, not for the activation of the hydrogen, but for the activation of the molecules with which the hydrogen has to react. If surfaces can be found as active towards these molecules as present available surfaces are with respect to hydrogen, tremendous improvements would be possible in the yields of ammonia and alcohol under much simpler operating conditions. The deuterium experiments indicate the direction which research in technical catalysis must take.

The study of enzyme reactions in heavy water is re-

vealing some of the reasons for the curious biological effects of this substance. Heavy water is not toxic in the way that carbolic acid or cyanide of potassium is toxic. Heavy water does, however, profoundly modify the speed of biological processes. Yeast ferments sugar in heavy water at only one ninth the rate in ordinary water, as was shown by Professor Pacesu at Princeton. Dr. J. Pace has found that the enzyme, catalase, present in the blood stream, and whose function it is to destroy hydrogen peroxide, does so at only half its normal speed when present in 85 per cent. heavy water. The most marked effects occur in the range of concentration from 85 to 100 per cent. deuterium, and this was the region found by Taylor, Swingle, Eyring and Frost for the marked toxic effects on fresh-water organisms. These results suggest that the biological effects may be the result of an upsetting of the delicate balance of the many chemical processes operative in all living systems. With the accumulation of larger supplies of the heavy water, arrangements are now being made to ascertain the effect of heavy water on the growth of cancer cells, a field of extraordinary interest.

Professor E. N. Harvey, of the biology department, has shown that heavy water (85 to 95 per cent.) does not prevent the luminescence of dried cypridina nor affect the luminescence of a fresh-water bacterium. It does diminish the luminescence of a marine form. It retards the growth of luminous bacteria, sometimes allowing slow growth without luminescence. The oxygen consumption of a salt-water luminous bacterium was reduced 60 per cent. in 86 per cent. heavy water, by 30 per cent. in 63 per cent. water and by 12 per cent. in 36 per cent. heavy water. The respiration of a fresh-water bacterium was less markedly affected. The curves relating reduction of respiration and concentration of heavy water would indicate zero respiration in 100 per cent. heavy water.

Heavy water was shown to kill a number of protozoa and rotifers but does not kill bacteria or injure *Euglena* irreversibly. It affects only slowly the protoplasmic rotation of *Elodea* cells and it has been shown to penetrate into such *Elodea* cells. In general Professor Harvey concludes that the action of heavy water may be likened to that of a generally unfavorable environment, leading to progressive changes in the cell. It would seem that the changes observed are the result of the differential effects on the rate of biochemical reactions already mentioned in connection with the enzyme reactions.

The reactions of heavy water with a variety of chemicals and of deuterium gas with other gases, at catalytic surfaces, such as nickel and copper, have resulted in a series of new compounds whose properties are now being studied. Thus, Professor Taylor

and Dr. J. C. Junger have succeeded in preparing the three ammonias containing, respectively, 1, 2 and 3 deuterium atoms, NH_2D , NHD_2 and ND_3 . Their existence is revealed in their characteristic absorption bands in the ultra-violet, each distinct and different from that of ordinary ammonia NH_3 . Their stabilities, when bombarded with atoms of excited mercury, are all markedly superior to that of ordinary ammonia. Professor G. Dougherty has similarly prepared a derivative of ordinary benzol in which one atom of hydrogen is replaced by one atom of deuterium to give the compound $\text{C}_6\text{H}_5\text{D}$. Professor R. N. Pease has prepared a derivative of the petroleum hydrocarbon, ethane, in which two atoms are of deuterium, the compound being $\text{C}_2\text{H}_4\text{D}_2$, whilst Professor Taylor and Mr. Smith have synthesized heavy methane CD_4 , in which all the atoms attached to carbon are deuterium atoms. This product has a density 25 per cent. greater than that of ordinary methane. The spectroscopy of all these compounds is of considerable interest.

A recent research by Rollefson in California indicates that chlorine atoms react about ten times more slowly with deuterium molecules than with hydrogen

molecules. In contrast with this result, data obtained by Dr. M. G. Evans in Princeton indicate that atomic deuterium and atom hydrogen react equally rapidly with oxygen to produce deuterium and hydrogen peroxides under the influence of excited mercury. The California results are in best agreement with Eyring's theoretical calculations of the effect of zero point energies of the two hydrogens on the rates of reaction. The results obtained by Evans permit a definite decision with regard to the mechanism of the reaction with oxygen. It is as an indicator in problems of reaction mechanism that deuterium is of the greatest utility in the field of reaction kinetics.

Professor R. W. Ladenburg, of the department of physics, has examined the heavy water for evidences of radioactivity. No positive evidence for such was found. The significance of this observation is that the smaller value for the mass of the neutron, as deduced from experiments in the University of California, would suggest that the deuterium atom was perhaps an unstable atomic system which might be liable to undergo spontaneous disintegration. The negative result favors therefore the higher value assigned to the mass of the neutron.

A MONUMENTAL REFERENCE WORK ON GEOGRAPHY

By Professor DOUGLAS JOHNSON

COLUMBIA UNIVERSITY

FOR some years there has been appearing in the French language a series of quarto volumes which should prove useful to a very wide circle of scientists and laymen. When the series is completed, it will constitute the great "Géographie Universelle," some twenty-two volumes grouped under fifteen titles, projected by the distinguished founder of the French school of geography, Vidal de la Blache, and published under the direction of the scholarly authority on historical geography, Lucien Gallois, of the University of Paris. It possesses importance for every man who would turn quickly to an authoritative, up-to-date, condensed account of the varied aspects—geological, geographical, climatic, botanical, zoological, economic and political—of different regions of the world.

NATURE OF THE ENTERPRISE

The undertaking, of which these volumes are the fruit, is admirable from every point of view. The conception of giving to the world a work which should replace the old "Géographie Universelle" of Réclus with a series of monographs not merely brought up to date but based on the modern scientific treatment of geography, is in itself excellent. It makes the enter-

prise something wholly new, instead of a mere revision of something old. The work is now far enough advanced to permit a judgment as to the manner in which the original conception is being executed.

The authorship of the various volumes is sufficient guarantee of the high quality of the work. The most distinguished leaders of the French school, some of them disciples of Vidal de la Blache himself, are cooperating to make the texts truly authoritative. For this task both the French conception of geography and the training of French geographers render these authors peculiarly competent. In the French view, geography is a synthesis of all the elements which give character and individuality to the various regions of the earth. To picture such a synthesis the French geographer must range widely in the fields of geology, climatology, botany, zoology, history, politics, sociology, economics. He specializes less narrowly and reads more broadly than is usually the case with his American geographical colleague. The French university system, with three lectures a week as the normal assignment of formal class instruction, and with less laboratory and other work than his American confrère performs, leaves the French professor leisure for study; while the practical necessity