

tween the rates of activation arising from the different zero-point energies of the bonds H—O and D—O in the hydrated ions.

Bowden and Rideal's measurement of the capacity of the Helmholtz double layer at the surface of mercury and other metals indicates a separation of about 1.5 Å. between the oxonium ions in the electrolyte and the negative charge on the cathode. This width of barrier together with a reasonable estimate of its height and shape indicates that leakage through the barrier is of secondary importance. On the other hand, the zero-point energy difference between a hydroxyl and a deuteroyl radical would make  $\alpha$  equal to 12; of course the actual force constant will not be the same in the ions as in the radicals, but the observed figures of about 6 are not inconsistent with the view that the separation is almost entirely due to the zero-point energy difference.

If the slow process at the cathode were the combination of atoms to molecules on the surface, there would again be a separation due to the zero-point energy, but the *maximum* values calculated for  $\alpha$  on this supposition are only about one-half the experimental values. Thus quite apart from arguments based on the magnitude of the constant in Tafel's overvoltage equation, it is clear that the slow process is not the combination of atoms, at any rate for these metals.

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#### FURTHER EXPERIMENTS ON THE PHYSIOLOGICAL EFFECT OF HEAVY WATER AND OF ICE WATER

Sir:

A previous communication [THIS JOURNAL, **55**, 4332 (1933)] reported greater longevity and less cell-disjunction in masses of *Spirogyra* in slightly concentrated deuterium oxide water of density 1.000061, which is in contrast to the lethal action of nearly pure H<sup>2</sup>H<sup>2</sup>O [cf. Lewis, *ibid.*, **55**, 3503 (1933); Taylor, Swingle, Eyring and Frost, *J. Chem. Phys.*, **1**, 751 (1933)]. The present report deals with short lengths of a filament of *Spirogyra nitida* in 5-cc. water samples exposed to northern light (temp. 10–14°). A representative filament of 31 cells in the isotope water had 43 cells after six days, of which 3 were dead; a filament of 37 cells in ordinary water showed no cell division at the end of six days and 20 cells died; in ice water renewed twice daily a filament of 50 cells showed 15 abnormal at the end of five days, while the filament in freshly condensed water renewed twice daily showed all of its 50 cells dead or shrunken in the same interval; the control filament (pond water) of this series had 47 cells initially and 64 normal cells after six days.

*Oscillatoria* spread more extensively in isotope water, possibly due to the  $P_H$  of 6.77 (kindly determined by Dr. T. L. Jahn with a glass electrode) for the difference was not as great in water samples buffered to 7.12.

The heavy water effects may be due to its influence on enzyme for a sample of pancreatic amylase in solution in the deuterium water for twenty-four hours was not as active in digesting starch as a similar portion in ordinary water (the erythro-dextrin stage was reached in eight minutes in isotope water and in six minutes in controls). In this case it is suggested that the hydrolysis is retarded by the deuterium apart from a  $P_H$  effect. Also, in fermentation tests a decrease of 10% in carbon dioxide production was observed when zymase was exposed for sixty-six hours to the isotope water.

Ice water may also condition enzyme action for Nord and Weiss [*Z. physik. Chem.*, **166**, 1 (1933)] report increased activity of enzyme solutions which have been frozen, possibly due to disaggregation of enzyme particles. Experiments by one of us (E. J. L.) in the Biology Department of Clark University show that oxidation of guaiaconic acid by the peroxidase-oxygenase system is increased if the solution is made up in freshly melted ice water and allowed to come to room temperature. When a solution of guaiaconic acid and peroxidase, without an oxygenase or peroxide, is frozen, oxidation occurs when the ice melts.

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### THE ISOTOPIC ANALYSIS OF WATER

Sir:

The spectral method which was used in the original discovery of deuterium is not capable of high precision. The oxides of the two hydrogens, however, have considerably different physical properties which afford a basis for precise analytical methods. Densities have been used extensively,<sup>1</sup> and we have found that the determination of the index of refraction by means of a Zeiss interferometer is simple, rapid, and very precise. We feel that our present experience with this instrument may be of value to other investigators.

The actual measurement is a difference in index of refraction between ordinary water and water containing higher concentrations of deuterium oxide. The instrument was calibrated for direct refractive index measurements by potassium chloride solutions and for molal percentage of deuterium oxide by comparison with the corresponding densities. One

(1) Gillfillan and Polanyi have developed an ingenious method based on the principle of the Cartesian Diver, *Z. physik. Chem.*, **166A**, 255 (1933).