placed further in the ultraviolet than are the corresponding bands of ammonia and have some structure on the short wave length side which is absent in corresponding ammonia bands. At longer wave lengths there are band systems not evident in the ammonia spectrum under similar operating conditions. The 68% product showed a larger number of these longer wave length absorption bands. It is possible that they may be associated with the presence in such preparations of the unsymmetrical molecule NHD_2. We are continuing these studies of absorption spectra and are extending them to the infra-red region. We are also extending the work in order to produce pure preparations of the mixed ammonias, the mono-deuteroammonia, NH_2D and the di-deuteroammonia, ND_2H. The chemistry of our products is also under study.

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ELECTROLYTIC SEPARATION OF HYDROGEN ISOTOPES AND THE MECHANISM OF THE CATHODE PROCESS

Sir:

Water containing approximately 7% deuterium was electrolyzed at 26° using platinum anodes and six different metals as cathodes, the electrolyte being potassium hydroxide initially 0.5 *N*. In addition, 0.5 *N* sulfuric acid was electrolyzed with cathodes of platinum and copper. The cathodic current density was 1 ampere per sq. cm. apparent area, but the surfaces were roughened with fine sandpaper. The extent of separation was determined by burning the hydrogen–oxygen mixture at a fine jet in a closed vertical Liebig condenser, collecting the water and measuring its density. All danger of explosion was avoided by inserting in the gas stream just above the jet a 10-cc. bulb filled with fine sand.

The ratio α of the specific rates of discharge is defined by the relationship $d \ln n_H = \alpha \, d \ln n_D$ where n_H and n_D are, respectively, the number of hydrogen and deuterium atoms in the electrolyte. The values obtained for α in the potassium hydroxide solution were: Pb 7.4, 7.2; Fe 7.6, 6.9; Pt 7.6, 6.5; Cu 6.8; Ni 5.5; Ag 5.3, 5.0. In the acid solution the values were: Pt 5.7, 5.7; Cu 5.5, 5.8.

The relation first given by Tafel connecting current and overvoltage has been interpreted by Volmer as showing that the slow process is the passage of a hydrogen ion over a potential barrier at the electrode surface, and Polanyi has suggested that this barrier is responsible for the isotope separation. The relative rates of discharge of the proton and deuton will depend upon two factors associated with the height and shape of the barrier, namely, the rates of leakage through the barrier, and the difference between 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 deuteroxyl radical would make α 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 α 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^2H^2O [*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.