

0.00546. The experiment was duplicated with heavy water of  $d_4^{20}$  1.06. The velocity coefficient was found to be  $k_1^1 + k_2^1 = 0.00290$ . From these results it can be concluded (1) that on solution in heavy water of a reducing sugar the displaceable hydrogen atom of that sugar is *immediately* replaced by a heavy hydrogen atom of the heavy water, and (2) that the mutarotation is indeed due to oxo-cyclo desmotropy, *i. e.*, to a change in which the double bond of a  $>C=O$  group is replaced by a ring formed by the migration of a hydrogen atom. The corresponding experiments with 100% heavy water will be carried out shortly.

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### THE DEUTEROAMMONIAS

*Sir:*

Three different samples of heavy water have been brought to reaction in the vapor phase with magnesium nitride to form ammonias in which the hydrogen atoms are predominantly of mass 2. The densities of the three products, relative to that of ordinary ammonia measured under the same conditions, were, respectively, 1.12, 1.158 and 1.174. Assuming equal equations of state for all the ammonias, these densities correspond to ammonias containing, respectively, 68, 90 and 99% of heavy hydrogen. The gases have the odor of ammonia. The physical properties show a progressive change with isotope concentration as is seen from the following data:

Percentage of heavy hydrogen	0	68	90	99
Freezing point, °Abs.	195.2	197.9	198.6	199
Boiling point, °Abs.	239.75	241.7	242.1	242.3

By means of a differential tensimeter using ammonia as reference the following vapor pressures were obtained for the 99% product:

$T$ , °Abs.	202.3	213	226.1	232.1	238.6
$P_{NH_3}$	77	184	364	511	714
$P_{ND_3}$	63	154	313	445	628

Assuming the latent heat of vaporization of ammonia to be 5797 cal. per mole at 1 atmosphere, the vapor pressure curve of the product gives a value for the latent heat of vaporization of  $ND_3$  of 5990 calories per mole.

With the assistance of Dr. G. I. Lavin we have examined the absorption spectra of the products in the far ultraviolet and found them to be similar to, but quite distinct from, that of ammonia, well defined spectrograms having been obtained. Densitometer curves made from our plates by Dr. Garman of New York University show that the principal bands are

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  $\text{NHD}_2$ . 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,  $\text{NH}_2\text{D}$  and the di-deuteroammonia,  $\text{ND}_2\text{H}$ . 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  $26^\circ$  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  $\alpha$  of the specific rates of discharge is defined by the relationship  $d \ln n_{\text{H}} = \alpha d \ln n_{\text{D}}$  where  $n_{\text{H}}$  and  $n_{\text{D}}$  are, respectively, the number of hydrogen and deuterium atoms in the electrolyte. The values obtained for  $\alpha$  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 deuteron 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 be-