

higher total pressures, disagreeing with the results of Steiner and Wicke [*Z. physik. Chem.*, Bodenstein Band, 817 (1931)], who concluded that the wall reaction is not very significant. Some preliminary measurements have been made at -79 , 0 and 99° by surrounding 20-cm. lengths of the recombination tube with appropriate baths. The results indicate a small but seemingly definite positive temperature coefficient corresponding to an apparent energy of activation of about 900 calories.

There are several reasons for believing that this is further evidence for the existence of a wall reaction. Eyring's [THIS JOURNAL, 53, 2537 (1931)] potential energy diagram for a three hydrogen atom system is to be interpreted as indicating a zero energy of activation for all possible gaseous trimolecular reactions involving hydrogen atoms and molecules. Reaction rates calculated with the use of kinetic theory diameters for the hydrogen atom and molecule, and assuming no energy of activation, yield reaction velocity constants that are only about half as large as the observed values and although the possibility of resonance interchange [Steiner, *Z. physik. Chem.*, B15, 249 (1932)] could increase the effective collision diameters several fold, it seems doubtful that these diameters could be as large as would be demanded by the introduction of the activation factor $e^{-900/RT}$

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SEPARATION OF THE ISOTOPIC FORMS OF WATER BY FRACTIONAL DISTILLATION

Sir:

With a twenty-foot fractionating column which has been shown to be equivalent to about forty theoretical plates [Henriques and Cornish, *J. Phys. Chem.*, 37, 397 (1933)], we have produced appreciable changes in the density of water by separation of the isotopes of hydrogen and oxygen. In our first experiment the ordinary isotopic composition was maintained at the bottom of the column. A stationary state was reached in two days, the water at the top showing a density diminished by 60 parts per million. In our second experiment the ordinary isotopic composition was maintained at the top of the column and samples were taken daily from the bottom. Conditions here were less satisfactory, owing to irregular flow. The density of the samples varied between 70 and 80 parts per million above ordinary water.

Even according to the first estimate [Lewis and Macdonald, *J. Chem. Phys.*, June (1933)] of the concentration of H^2 in ordinary water, which we now believe to be altogether too high, the loss of all the H^2 in the first experiment would cause a diminution in density of only 17 parts

per million. Assuming that the amount of O^{18} in ordinary water causes a density difference of 175 parts per million, these experiments indicate that the concentrations of O^{18} at the bottom and top of the column are nearly in the ratio 3 to 2, but do not show to what extent H^2 is concentrated. To answer this question Lewis and Macdonald are measuring the vapor pressure of water containing different amounts of H^2 . With water in which 66% of the hydrogen is H^2 the vapor pressure is below that of ordinary water by 3.5% at 100° and by 8.8% at 25° .

These large differences would at first sight indicate that large separation can be obtained by fractional distillation, but the system presents certain novel features. Consider the three species H^1H^1O , H^1H^2O and H^2H^2O . As a first approximation we assume that the three partial vapor pressures, p_{11} , p_{12} , p_{22} , are proportional to the mole fractions in the liquid, N_{11} , N_{12} , N_{22} , and further that there is a random distribution of the hydrogen atoms among the oxygen atoms so that $p_{12}^2 = 4p_{11}p_{22}$ and $N_{12}^2 = 4N_{11}N_{22}$. It follows that if y is the atomic ratio of H^2 to H^1 , and the vapor pressures of pure H^1H^1O and H^2H^2O are a^2 and b^2 , then $N_{11}:N_{12}:N_{22} = 1:2y:y^2$ and $p_{11}:p_{12}:p_{22} = a^2:2aby:b^2y^2$. Hence the equation for the total vapor pressure is $P = (a + by)^2/(1 + y)^2$. Or if x is the atomic fraction, $y/(1 + y)$, then $P^{1/2} = a - (a - b)x$. It is not the vapor pressure, but its square root, that is a linear function of the atomic fraction. Similarly, if y' is the atomic ratio in the gas, $y'/y = b/a$ (not b^2/a^2). While, therefore, these calculations are not favorable to a large fractionation of the hydrogen isotopes at atmospheric pressure, it appears that fractional distillation under reduced pressure should be effective, and this experiment is now under way.

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NEW BOOKS

Hommage a Henri Moissan, 4 Octobre 1931. Published by *Chimie et Industrie*, Société de Chimie Industrielle, 49 Rue des Mathurins, Paris VIII^e, France, 1932. 93 pp. Illustrated. 23 × 28.5 cm.

A monument and a plaque in memory of Henri Moissan were unveiled on October the 4th, 1931, at the Municipal College in Meaux. It was here that Moissan received his early education.

This volume contains an excellent account by Paul Lebeau of Moissan's life and scientific achievements, a bibliography of Moissan's publications, a description of the