The Diffusion of Hydrogen Through Metals: Fractionating the Hydrogen Isotopes

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LETTERS TO THE EDITOR

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The Diffusion of Hydrogen Through Metals: Fractionating the Hydrogen Isotopes

In the summer of 1930 a striking example of the diffusion of hydrogen through metals was observed. The diffusion of the hydrogen took place under the following conditions. Two pieces of steel sheet metal, each about 1/32" (0.75 mm) thick, were welded together carefully at the four edges and immersed as cathode in an acid solution (mixture of sulfuric and hydrochloric acids). The temperature of the acid bath was about 70°C. The current density employed was about 22 amperes per dm². At the end of two hours a very marked bulging of these sealed plates or iron "pillow" was observed. Thereupon the seal was broken and the gas collected over water and tested. The clear, sharp explosion that was obtained showed the presence of hydrogen. This experiment was repeated several times and always the same results were obtained. We decided to determine whether or not the hydrogen thus collected within the metal "pillow" was substantially the lighter of the two hydrogen isotopes.

Preliminary qualitative experiments were carried out with tubes of iron, nickel and palladium. The walls of the iron tubes were about 0.8 mm thick, those of the nickel 0.2 mm and 0.4 mm respectively, and those of the palladium about 0.25 mm. The baths used were: a 25 percent (by volume) sulfuric acid solution, a 10 percent NaOH solution (by weight), and a 25 percent $MgSO_4 \cdot 7H_2O$ solution (by weight). The temperature varied from 85 to 90°C. The current density employed varied from a little less than 11 amperes per dm² to over 120 amperes per dm². The anode used was platinum. The gas passing through the walls of the tubes was collected over water. The palladium tube gave the best performance. A 25 percent sulfuric acid solution was used and the gas gave a clear test for hydrogen.

An apparatus was then set up whereby the hydrogen passing through the palladium tube wall could be "burned" and the resulting water collected. The electrolyte consisted of special water containing about ½ percent "heavy water," to which was added fuming sulfuric acid, in the proportion 335 cc special water, to 25 cc fuming sulfuric acid. During the electrolysis the volume of the solution was kept constant. The temperature was maintained at about 85°C. A current density of 60 amperes per dm² was employed. The voltage drop was 4.3 volts. A platinum anode was used. The length of the palladium tube immersed in the electrolyte was 25 cm. At the end of 28 hours, about 2 cc of water had collected. Its specific gravity was found to be 1.00020. This would indicate that neither light nor heavy hydrogen *alone* passed through the walls of the palladium tube, but a mixture of both.

An experiment was then arranged to determine the rate at which hydrogen passed through the walls of the palladium tube used in the preceding experiment. The tube was carefully cleaned. A new solution was used consisting of distilled water 75 percent by volume; c.p. sulfuric acid 25 percent by volume. The temperature of about 70°C was maintained for each run. The experiment was continuous, that is, with change of current density the apparatus and solution were left undisturbed. The volumes of gas were collected under as similar conditions as possible. The temperature of the water, over which the gas was collected, was 20.5°C. The barometric pressure was 766.4 mm. The data are given in Table I.

TABLE I.

Current density amp./dm²	Voltage	Volume gas collected cc	Time min.	Volume gas per minute cc
100.	7.5	1000	48	20.8
50.	5.2	430	120	3.5
20.	3.2	60	60	1.0

Another experiment was run to determine whether oxygen would diffuse through the walls of this same palladium tube. The same electrolyte was used as in the preceding experiment. A temperature of 40°C was maintained. A current density of 100 amp. per dm² was used. The cathode was platinum. No gas was observed to come through the tube even after 2½ hours. During the run, however, a dark violet-colored film was observed on the

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surface of the tube. That film might have acted to prevent the diffusion of the oxygen through the walls of the tube.

These preliminary experiments show that with the palladium cathode fractionation of the two isotopes does occur, protium, the lighter isotope, diffusing through more readily. The experiments with the iron "pillow" indicated that we are dealing with extraordinary high pressures. On the basis of the overvoltages involved, a simple calculation indicates that these pressures or the fugacities are of the order of a million atmospheres.

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        January 3, 1934.

Isotopic Fractionation of Hydrogen

Water containing approximately one part deuterium to 200 parts of protium was electrolyzed with a current of one ampere and the hydrogen produced was passed over copper oxide at a temperature of 200°C. The rate of flow of the hydrogen was such that roughly 50 percent of it was converted into water and the remainder was forced over copper oxide at about 600°C, so that at the high temperature all the hydrogen reacted to form water. The two fractions of water, 10 ml each, were condensed separately, and distilled into pycnometers calibrated at 25°C. The sample of water formed at 200°C had a mass of 6.6 mg less than the 10 ml formed by the complete combustion.

The experiment was repeated using two cells in series so that the rate of flow of hydrogen was twice as great and the surface of copper oxide was kept the same. (80 g of copper gauze, number 26 wire, was used in each reaction chamber.) This time the light fraction of 10 ml weighed 5.0 mg less than the heavy fraction. The samples of water were interchanged in the pycnometers and identical mass differences were found.

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        January 11, 1934.

Unimolecular Decomposition at High Pressures[1]

A recent letter by Coffin and Geddes[2] states that the first order coefficient for the decomposition of paraldehyde decreases by 50 percent when the pressure is increased from a few mm to 18 atm. They suggest as an explanation that the reactive degrees of freedom lie in the center of the molecule and are not excited directly by collisions; it is supposed that the probability of reaction per unit time will therefore increase when an activated molecule is undisturbed. In considering this mechanism it will be helpful to adopt the usual convention that the actual reaction may be mentally suppressed without otherwise changing the behavior of the molecule. States for which some small group of internal vibrations has at least a critical energy decompose spontaneously when the convention is relaxed; while it is maintained, they are present at the Maxwell-Boltzmann quota. Coffin and Geddes make the plausible-sounding assertion that the rate at which these states are produced is less at high pressures; to maintain the same equilibrium, however, it would be necessary for the rate at which such states are destroyed to decrease to the same extent. It seems impossible to believe that the occurrence of collisions could prevent the central degrees of freedom from losing energy. A closer understanding of the fallacy is perhaps obtained by means of the following simple model; the molecule has three degrees of freedom, A, B and C; only A is directly affected by collisions, and A is connected with C only through the intermediary B; the probability that a quantum of energy will be transferred from A to B, B to A, B to C or C to B is k sec.$^{-1}$. It is then readily shown that if A is given a quantum when B and C have none, the chance that C has the quantum at the expiration of time t increases initially as $(kt)^2/2$, and it would seem that such a model gives the Coffin-Geddes effect. This is not so, however; the collision will have no influence unless the quantum is at A, since only A participates in collisions; if the quantum is at A, the deactivation which occurs is perfectly balanced by activation of A in some other molecule. In general, it will be true that if collisions cannot directly excite some special vibration, they cannot directly quench it either.

LOUIS S. KASSEL[3]

U. S. Bureau of Mines,
    Pittsburgh Experiment Station,
        Pittsburgh, Pennsylvania,
            January 12, 1934.

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[2] C. C. Coffin and A. L. Geddes, J. Chem. Phys. 2, 47 (1934).

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Thermal Decomposition of Deuterium Iodide

We have previously pointed out[1] that the thermal dissociation of hydrogen iodide should be dependent on the concentration of deuterium in the hydrogen iodide. Experiments in this laboratory have verified these theoretical calculations.

Hydrogen iodide was prepared from its elements and purified by three vacuum distillations. The reaction vessel

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[1] H. C. Urey and D. Rittenberg, J. Chem. Phys. 1, 137 (1933).