

Unimolecular Decomposition at High Pressures

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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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Unimolecular Decomposition at High Pressures¹

A recent letter by Coffin and Geddes² 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 $k \text{ sec.}^{-1}$. 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.

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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 out¹ 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

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

was filled to about 60 cm pressure and sealed off. The reaction vessel was kept at the chosen temperature for a period about 15 times longer than would be necessary for ordinary hydrogen iodide to attain equilibrium. The reaction vessel was then pumped out through a break seal and the iodine and hydrogen iodide frozen out in traps with liquid air. The iodine and hydrogen iodide were dissolved in water and the solution analyzed for I_2 and H^+ . At no time were the gases in contact with anything but glass. The fraction decomposed, h , was calculated from the equation

$$h = 2[I_2]/(2[I_2] + [HI]),$$

where $[I_2]$ is the moles of I_2 at equilibrium, and $[HI]$ the moles of HI at equilibrium. The results are given in Table I. h_B is the value Bodenstein² gives for ordinary hydrogen iodide. Δh is the difference in the fraction decomposed of the sample rich in deuterium iodide and pure protium iodide.

The concentrations of the 13.5 and 40.0 percent samples were determined by W. Bleakney on his mass-spectrograph.³

TABLE I.

Conc. H^2	h exp.	h calc.	Δh exp.	Δh calc.
$T = 398^\circ C$				
0.0%	0.20719	—	$h_B = 0.20703$	
13.5	0.20838	0.20878	0.00119	0.00175
$T = 468^\circ C$				
0.0	0.22724	—	$h_B = 0.22772$	
40.0	0.23287	0.23326	0.00563	0.00602
72.1	0.23877	0.23904	0.01153	0.01180

The concentration of the 72.1 percent sample was determined by burning 500 cc of hydrogen iodide and determining the concentration of deuterium in the resultant water by the interferometric method which will be published shortly by Crist, Murphy and Urey. They assume that the molecular volume of deuterium oxide is the same as protium oxide. However, if the mol volume is that claimed by G. N. Lewis, the concentration of the sample will be about 76.5 percent. A change of 1 percent in the concentration of the deuterium will change Δh by 0.00013. This uncertainty will, however, not apply to the 13.5 and 40.0 percent samples since the concentrations were determined by the mass-spectrograph. It is to be noted that all our Δh 's are lower than those calculated. It is doubtful, however, if this is significant since we estimate that our experimental error is about 0.00040 in Δh . If we assume that our concentration of deuterium in the last sample is 76.5 percent then the difference between the Δh exp. and Δh calc. will be about 0.00084. This seems to be definitely larger than our experimental error.

While this experiment was conducted in the gaseous phase there is no reason to doubt that similar deviations from the classical value of the equilibrium constant will be found for reactions in condensed systems.

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January 15, 1934.

² M. Bodenstein, Zeits. f. physik. Chemie **29**, 295 (1899).

³ Bleakney, Phys. Rev. **34**, 157 (1929); **39**, 536 (1932).

Heavy Water Inert, Due to Low Association

Lewis and MacDonald¹ have reported the viscosities of heavy water over a considerable range of temperature. The very important question arises as to the effect of the extra proton in the nucleus of hydrogen upon the associ-

ation of water. Bingham and Spooner² have given the temperature constants for ordinary hydrogen and for oxygen at 50, 100 and 200 rhes, as reproduced in Table I. As fluidities have been found to be additive, the temperature required to give ordinary water a fluidity of 200 rhes would be 131.6°K, provided that the water remained unassociated. As shown in Table I, the observed value (328.9°K) is very much higher, leading to an association of 2.50.

The fluidity of heavy water is quite different from the fluidity of ordinary water, so that it is necessary to conclude that the additional proton affects the fluidity of water and presumably therefore the temperature constant of fluidity. (See Fig. 1.) If this is so, the simplest assumption is that the effect is additive, so that if the constant of hydrogen is 59.3 at 200 rhes the constant for deuterium is 118.6°, for the same fluidity. This would lead to a higher calculated temperature of 250.2° required to give deuterium oxide a fluidity of 200 rhes, again on the *proviso* that the water in question is non-associated. This is in accordance with the observed fact that heavy water is more viscous than

TABLE I.

	50 rhes	100 rhes	200 rhes
Hydrogen temperature constant (Bingham and Spooner)	45.9	50.4	59.3
Oxygen temperature constant	13.9	13.6	13.0
Observed temperature K for ordinary water	269.7	293.3	328.9
Calculated temperature K for ordinary water	105.7	114.4	131.6
Association of ordinary water	2.55	2.56	2.50
Deuterium temperature con- stant	91.8	100.8	118.6
Observed temperature K for deuterium oxide	277.8	301.7	(336.7)
Calculated temperature K for deuterium oxide	197.5	215.2	250.2
Association of deuterium oxide	1.41	1.40	(1.34)

¹ Lewis and MacDonald, J. A. C. S. **55**, 4730 (1933).

² Bingham and Spooner, J. Rheology **3**, 221 (1932).