

## The Equilibrium Between the Three Hydrogens

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tribution throughout the contributory degrees of freedom of a molecule is equally probable no effect of shortened mean free time (i.e., increased pressure) on reaction rate is to be expected since the particular distribution favorable to reaction is as probable as any other. If on the other hand the distributions most probable on collision are not coincident with those favorable to reaction a definite time interval must elapse between activation and decomposition due to the fact that different distributions follow one another at a finite rate. If such be the state of affairs therefore, the longer any one activated molecule is left alone the greater is the probability that it will react; that is to say the shorter the time between collisions (i.e., before deactivation) the smaller the chance of reaction. In other words increase of pressure may be expected to retard the reaction to an extent which is dependent upon the effectiveness with which the "vital" degree of freedom is protected and which will vary inversely as a linear function of the pressure.

This effect is to be expected particularly in the case of complex symmetrical molecules such as the paraldehydes<sup>1, 2, 4</sup> whose vital degrees of freedom lie well within the periphery presented by the rotating molecule to its

colliding neighbors. Unfortunately in no case is it yet possible to estimate the necessary minimum time interval between the receipt and expenditure of activation energy and to compare its order of magnitude with that of the mean free time. Times of atomic relaxation however are known to be of the order of  $10^{-8}$  sec.—an interval certainly longer than mean free times at pressures of one atmosphere or more—and vibrational excitation and its consequences might be expected to be more sluggish than electronic. Indeed the insulators suggested by O. K. Rice<sup>5</sup> (see also<sup>6, 7</sup>) will account for practically any time lag required.

Other reactions are being examined for this effect.

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<sup>4</sup> Coffin, Can. J. Research (In press).

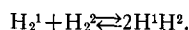
<sup>5</sup> Rice, Zeits. f. physik. Chemie **B7**, 226 (1930).

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<sup>7</sup> Coffin, Trans. Roy. Soc. Can. 1933 (In press).

### The Equilibrium Between the Three Hydrogens

While studying the dependence of the equilibrium of the hydrogen-iodine reaction on the isotopic composition of the hydrogen,<sup>1</sup> it has been necessary to check the composition of the hydrogen by the mass-spectrographic method.<sup>2</sup> A sample of the hydrogen iodide used in this work was decomposed by allowing it to react at ordinary temperatures with mercury. Two other samples were the hydrogen produced by the decomposition of hydrogen iodide at 397°C and at 468°C. In determining the deuterium-protium ratio, the relative abundances of the three varieties of hydrogen molecules, H<sub>2</sub><sup>2</sup>, H<sup>1</sup>H<sup>2</sup> and H<sub>2</sub><sup>1</sup> were determined, thus permitting a determination of the equilibrium constants for the reaction,



The equilibrium constant of this reaction has been calculated<sup>1</sup> and thus a check against theory can be secured.

Three samples were analyzed, check determinations being made on each. The results are summarized in Table I.

TABLE I.

Sample	T	Run	H <sub>2</sub> <sup>2</sup>	H <sup>1</sup> H <sup>2</sup>	H <sub>2</sub> <sup>1</sup>	K (obs.)	K (calc.)
5A	25°C	1	1.00	20.8	132	3.28	3.28
		2	1.00	21.2	137	3.28	
5B	397°C	1	1.00	13.9	46.0	4.20	3.73
		2	1.00	12.6	47.4	3.35	
6B	468°C	1	1.00	2.70	1.91	3.82	3.82
		2	1.00	2.68	1.96	3.68	

The numbers given under the headings H<sub>2</sub><sup>2</sup>, H<sup>1</sup>H<sup>2</sup>, and H<sub>2</sub><sup>1</sup> give the relative abundances of the three molecules. At the time 5B was analyzed, the apparatus was fluctuating rather badly. The cause was later traced to variations in the magnetic field. When this trouble was remedied, much more reliable results were secured for 6B. In each case the observed equilibrium constant agrees closely with the calculated values. These are secured by interpolation from the tables previously published.

Samples 5B and 6B were prepared at the temperatures recorded in the table but remained in all glass containers at room temperatures for about twenty-one days before analysis. The fact that the equilibrium constants are those characteristic of the temperature of preparation shows that the exchange reaction does not take place rapidly, and thus that this reaction is similar to the exchange reaction between hydrogen and steam investigated by Crist and Dalin.<sup>3</sup> The time between preparation and analysis is not so long as that in the observations on liquid water and hydrogen by Oliphant,<sup>4</sup> and perhaps the method of analysis is not so sensitive.

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

<sup>2</sup> W. Bleakney, Phys. Rev. **41**, 32 (1932). H. S. Taylor, H. A. Gould and W. Bleakney, Phys. Rev. **43**, 496 (1933).

<sup>3</sup> R. H. Crist and G. A. Dalin, J. Chem. Phys. **1**, 677 (1933).

<sup>4</sup> M. L. Oliphant, Nature **132**, 675 (1933).

Also, the agreement between experiment and theory gives reasons for confidence in the mass-spectrographic method of analysis. This method depends on two assumptions. The first is the very reasonable one that the probability of ionization is the same for all three hydrogen molecules and these results are in agreement with that assumption. The second is that the equilibrium is not appreciably disturbed by the process of analysis, an assumption which has been investigated and shown to hold for the high rate of flow through the apparatus which was used here. The pressure and electron velocity were, of

course, adjusted so that monatomic and triatomic ions were entirely negligible.

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